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MINOR ELEMENTS IN GOLD.

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ABSTRACT.

Minor amounts of many elements occur in gold. These minor elements vary greatly in gold taken from different districts. These differences can more readily be related to metallogenetic zones or provinces than to any difference in the type of deposit in which the gold is found. In most cases these minor elements are believed to be chemically rather than mechanically included in the gold.

Preliminary results also suggest that after more thorough and detailed work it may be possible, by means of spectrographic analysis, to determine the metallogenetic province or zone, and in some cases even the mine, from which a particular sample of gold originates.

INTRODUCTION.

DURING recent years there has been an intensive search for strategic minerals in British Columbia and the Yukon. One of the tools which has been employed in this search is the spectroscope, and with it some valuable results have been obtained. Perhaps the most immediately useful of these results has been the outlining of several metallogenetic provinces or zones, each of which is characterized by a particular assemblage of elements. It is now possible to state with some degree of assurance that some of these metallogenetic zones are good areas in which to prospect for tin, others for mercury, and still others for cadmium-bearing sphalerite, or for platinum and palladium respectively.

In this search for strategic elements many minerals are used as "pathfinders," a term transplanted from more martial fields, but indeed equally appropriate and self-explanatory in this. Sphalerite,

galena, tetrahedrite, stibnite, pyrrhotite, pyrite, arsenopyrite, and various silicates have been tried out in the role of "pathfinder." To achieve success as a "pathfinder" a mineral must possess two qualifications: it must tend to carry with it, either in chemical or mechanical association, the elements for which a search is being made, and it must be readily recognizable by a prospector. This second qualification although not essential is desirable because it is possible to achieve maximum results only if the prospectors and the mineralogists and geologists can cooperate satisfactorily. One of the chief tools of the prospector is the gold pan and all prospectors can be expected to find gold with this pan, even if the gold is present in small amounts. Consequently, it was natural that we should investigate the possibilities of using gold as a "pathfinder." Gold has limitations as a "pathfinder" and one of the most obvious limitations is that it does not occur in all the areas in which investigations are to be made. Fortunately gold, in small amounts, is found in a great many areas in British Columbia and consequently it has proved to have some value in the search for strategic elements, particularly tin.

Incidental to the general work, gold from twenty-six British Columbia and Yukon occurrences has been spectrographically analyzed. These analyses were primarily qualitative, although they are presented in a semi-quantitative manner.

The results submitted in this paper are suggestive although naturally, with such a small number of samples analyzed, inconclusive. Already these results have had practical applications—the finding of tin in place and the identification of stolen gold—and we are submitting them now in the hope that further interest may be stimulated in the possibilities of using the spectroscope not only in the practical field of prospecting, the detection of salting, and the identification of gold, but also in the more fundamental studies relating to the origin of ore deposits.

PROCEDURE

The determinations were recorded on 2 in. by 10 in. Eastman type II F. (Tropical) plates, which have a useful range between

2,200 and 6,800 A, from arc excitation through a medium Hilger quartz spectroscope. Each "shot" consisted of impressing on a plate, by means of a Hartmann diaphragm, a series of tangent narrow strips comprising the successive spectra of: (1) a tin standard (from C. P. tin), (2) the gold sample arced for sixty seconds, (3) the gold sample arced for ninety seconds beyond the sixty seconds, (4) the iron arc (from Hilger's "spec pure" iron rods). In order to check on the purity of the carbons and to insure against electrode contamination, every plate negative had impressed on it a spectrum of the empty carbon electrodes. A tin standard was "shot" because tin happened to be the most sought after element during this investigation. A wave-length scale was also reproduced with each "shot" and this scale, together with the tin and iron spectra, made it possible to measure the lines present with considerable accuracy. Hilger's charts of the iron spectrum and of the arc spectrum of R. U. Powder showing the "Raies Ultimes" of the elements together with Brode's [1] spectrum charts were used to identify lines. The Massachusetts Institute of Technology Wavelength Tables which cover all data of known accuracy, were also found extremely valuable. Whenever necessary, a direct visual comparison was made between an unknown line or lines with those on a standard plate of the suspected elements.

The work was originally planned as largely exploratory and consequently no serious attempt was made to obtain quantitative results. However, chiefly on the basis of numerous assays and on the comparative strength of particular lines, a distinction has been made of the amount of minor elements present on the basis of their being S (strong $+0.5\%$), M (medium $+0.1\%$ -0.5%), and F (faint -0.1%). In general these strengths, although of doubtful absolute accuracy, are, for the elements being discussed, of value for comparative purposes, and should be interpreted only on this basis.

[1] Brode, W. R.: Chemical Spectroscopy. John Wiley and Sons, Inc., New York, and Chapman and Hall, Ltd. London. 1933.

THE RESULTS.

Table I gives the results secured from twenty-six specimens from the Yukon and British Columbia. It will be noted that all the Yukon samples, with one exception, came from placers. The British Columbia samples, with one exception, were all taken from lode deposits.

GENERAL REMARKS.

Many elements found in the analyses, such as silica, alumina, sodium, calcium and magnesium, are not reported. Their presence may be accounted for in most instances by mechanically locked gangue such as quartz. The elements listed above in Table I could, however, be present either as mechanical inclusions or chemically combined in the gold. In the latter case the minor elements might be present either as an alloy or as a solid solution.

However, although occasionally it was not possible to remove all the non-metallic lustered gangue, every effort was made to select samples free from all metallic lustered or dark colored gangue. Crook,[2] who previously made spectrographic analyses of native golds, came to the conclusion that, of the many elements present in native golds, copper, silver, and iron are always present. Our work confirms this conclusion. Crook, speaking of other elements, many of which are listed in Table I, says that "it is difficult to determine whether these elements are in the form of metallic inclusions analogous to the manganese sulphide that occurs in all steel." It is possible that some elements are present mechanically and some chemically combined. The following factors, which apply equally to the golds in Table II, suggest that the bulk of these minor elements are chemically combined with the gold.

Evidence which suggests that some of the

Minor Elements are Chemically Associated with the Gold.

(1) A minute amount of iron is present in all samples. This is the case whether the gold is selected from a deposit rich or poor

[2] Crook, W. S.: Preliminary spectrographic and metallographic study of native gold. A. I. M. E. Met. Techn., Feb., 1939, T. P. 998.

TABLE I.

YUKON AND BRITISH COLUMBIA GOLD.

TABLE I.

YUKON AND BRITISH COLUMBIA GOLD.

Note: S = Strong +0.5%
M = Medium +0.1 − 0.5%
F = Faint −0.1%.

No.	Locality.	Type of deposit.	Ag.	Cu.	Fe.	Mn.	V.	Ti.	Hg.	Pb.	Bi.	Te.	As.	Sb.	Zn.	Cd.	Sn.	Pd.	Pt.
1.	Dublin Gulch, Yukon Ty.	P	S	M	F	F	F	F	F	F	M		M	F	F		F		
2.	Highet Creek, Yukon Ty.	P	S	M	F	F	F	F	F	S	M		M	F	F		F		
3.	Highet Creek, Yukon Ty.	P	S	M	F	F			F	F	M		M	F	F		F		
4.	Minto Lake, Yukon Ty.	P	S	M	F				F										
5.	Arizona Creek, Yukon Ty.	P	S	M	F	F		F	F	F				F	F		F		
6.	Ledge Creek, Yukon Ty.	P	S	F	F		F	F	F	F							F		
7.	Canadian Creek, Yukon Ty.	P	S	M	F	F	F	F	M	F	M	F		F	F	F	F		
8.	Hunker Creek, Yukon Ty.	P	S	M	F		F	M											
9.	Bonanza Creek, Yukon Ty.	P	S	F	F			F											
10.	Klondike Valley, Yukon Ty.	P	S	F	F			F											
11.	Dominion Creek, Yukon Ty.	P	S	M	F		F	F		F									
12.	Gold Hill, Wheaton, Yukon Ty.	M?	S	F	F			F	F										
13.	Usk, B. C.	M	M	F	F		F	F	M		M	F	F	S		F	F		
14.	Hedley, B. C.	C	S	F	F	F	F	F	F		M		F		F	F	F		
15.	Copper Mountain, B. C.	C	S	M	F	F	F	F	M					F			F	M	F
16.	Pioneer, B. C.	M	S	F	F	F	F	F	F								F		
17.	Bralorne, B. C.	M	S	F	F			F	F								F		
18.	Coronation Group, B. C.	M	S	F	F			F	F										
19.	Cariboo Gold Quartz, B. C.	M	S	F	F			F	F		F								
20.	Williams Creek, Cariboo, B. C.	P	S	M	F	F			F	F									
21.	Privateer, V. I., B. C.	X	S	M	F			F	F	F			F						
22.	Barnacle, Zeballos, B. C.	X	S	M	F	M					S	M			F		F		
23.	Texada Gulf, B. C.	?	S	M	F	F		F	F	F									
24.	Camp McKinney, B. C.	M	S	M	F					F	M		M						
25.	Premier (Electrum), B. C.	E	S	S	S	M			Tr?	S			F	F			F		
26.	Topsy, B. C.	M	S	M	F		F	F	F	S			F	F		F			

Note: The types of deposit are indicated by symbols. However, much of the evidence is second-hand and corrections will be welcomed. The authors realize fully that the time and temperature at which gold is despoited in a vein may differ considerably from the time and temperature at which the vein is deposited. The authors do not discuss the problem of varying compositions in different periods of vein deposition because they believe that this can only be usefully discussed when much more information is available. P = Placer. E = Epithermal. M = Mesothermal. H = Hypothermal. C = Contact metamorphic. X = Xenothermal. ? = not sufficient evidence.

in iron-bearing minerals. In many samples, notably those from the Lillooet Division of B. C., gold was selected from samples containing only gold and quartz. No other potential iron-bearing mineral was observed, even though several polished sections were examined. Iron was present in these samples in approximately the same amounts as it was in samples taken from ores rich in iron-bearing minerals. The same is true with silver and copper.

(2) Cadmium and zinc are commonly associated. British Columbia sphalerite usually carries from 0.2 to 0.8 per cent cadmium. Fourteen gold samples contained cadmium and only three of these showed any zinc.

(3) Bismuth and lead are frequently found together in the Cariboo Division of B. C., usually in the form of cosalite and galenobismutite. Spectrographic analyses of these minerals also show traces of tellurium. However, numerous polished sections of ore taken from the Cariboo Gold Quartz Mine in the immediate vicinity of the selected gold samples have failed to show galena, bismuthinite, or native bismuth. Yet the gold analyzed from the mine shows bismuth but neither lead nor tellurium. A sample of placer gold from Williams Creek shows lead but no bismuth! Bismuth and tellurium are found as joseite, or a closely related mineral, at Hedley. Native bismuth but no native tellurium occurs in this area; yet bismuth is found in the Hedley gold and not tellurium. It is interesting to observe, and it may be significant to note, that in every case where tellurium is found in a gold, either bismuth or lead, or both, are also present. The lead telluride and the several bismuth tellurides are frequently found associated with gold, the bismuth tellurides being known in several British Columbia Districts. This might indicate a mechanical association.

(4) Tin, mercury, and zinc minerals are restricted in number and are recognizable with relative ease. Careful examination of the selected samples enables the authors at least to feel reasonably confident that the association of these elements with gold is not a mechanical one.

(5) Crook draws attention to the work of Rose and Newman [8] who say in part as follows: "Gold is occasionally found alloyed with copper and sometimes also with iron, bismuth, lead, mercury, tin, antimony, palladium, or rhodium." Possibly this conclusion, together with the fact that no palladium or antimony minerals have yet been seen intimately associated with the gold samples which were analyzed, suggests a chemical rather than a mechanical association.

OCCURRENCE OF ELEMENTS PT, AS, V, MN, AND TI.

The manner in which the remaining elements—platinum, arsenic, vanadium, manganese, and titanium—occur, is doubtful. Titanium is almost as widespread as iron, silver, and copper: it is present in fifty-three out of sixty-six analyses. Manganese, vanadium, and arsenic are of common occurrence, but platinum is rare. Because of the care taken to ensure freedom from physical contamination by minerals likely to contain these elements, and because, in addition, more than one "shot" was frequently taken of gold from a specific mine, and in some instances "shots" were taken of samples collected at various times from different parts of a mine, the authors incline to the belief that these elements also are chemically combined with the native gold. However, there is no doubt that much more conclusive evidence must be forthcoming before the matter may be considered closed.

DISTRIBUTION OF MINOR ELEMENTS IN VARIOUS TYPES OF DEPOSIT.

Obviously, with so few samples, it would be unwise to do more than generalize on the distribution of these minor elements. However, even with this reservation, one conclusion may be drawn. The type of deposit may affect, but it does not control the minor element content of the gold.

Mercury occurs alike in gold from Privateer (xenothermal), Bralorne (mesothermal), Hedley (contact metamorphic), and it has been doubtfully identified in Premier gold (epithermal).

[8] Rose, T. K., and Newman, W. A. C.: The Metallurgy of Gold. Griffin and Co., London, 1937. Pp. 90–91.

Tin, likewise, is in gold from every type of deposit, although it does occur more consistently in the high temperature types.

Tin is generally considered as a high temperature mineral and mercury as a low, so their joint presence in many of these gold analyses may be taken to imply that this association may be explained by their occurrence in a metallogenetic zone rather than because they are in a particular type of deposit. This association also implies a chemical rather than a mechanical connection with the gold. It also may be argued that the reason for this association between mercury, tin, and gold is that they all originated from a common source and the gold was deposited at more or less the same temperature, irrespective of the nature of the deposit as a whole in which the gold occurs.

Vanadium also is found with gold from widely different types of deposit, but it is lacking in some mines, notably in the Clayoquot (Zeballos Mines), Cariboo, and Greenwood areas. No particular significance would be attached to the absence of vanadium in these areas but for the fact that out of eighteen sphalerites examined from these same areas, only one showed even a trace of vanadium.

The presence of titanium in gold seems to be so wide-spread that its absence in a particular gold is of more interest than its presence.

Manganese is found in many golds and its presence may be of significance because of the part ascribed to it by some in the solution and transportation of gold.

USEFUL APPLICATIONS OF SPECTROGRAPHIC ANALYSES OF GOLD.

A. Gold Identification. Possibly the most interesting of all the minor elements so far observed in British Columbia are platinum and palladium. Platinum and palladium occur in Copper Mountain gold. Copper Mountain is one of the two important copper-producing mines in British Columbia, but it produces some gold as a by-product. Palladium was first reported by Matthews [4] in

[4] Matthews, W. H.: The spectrochemical analysis of some native golds and silvers from Western Canada. Unpublished Essay. Dept. of Geology, University of British Columbia, 1941.

1941, and this information was duly conveyed to the Granby Company, which operates Copper Mountain. Some time later, gold was stolen from the Copper Mountain mill. The stolen gold was in the possession of a defendant, but in order to prevent any recurrence of this type of theft, the company was most anxious to obtain a conviction. In order to obtain a conviction it was vital for the company to substantiate its claim, namely, that the gold found in the possession of the defendant was indeed gold from Copper Mountain and not, as the defendant alleged, gold from a different place. At this stage in the proceedings, the company recalled the fact that their gold had been reported to contain the minor elements palladium and mercury. Samples of the allegedly stolen gold were sent for comparison with more of the Copper Mountain gold. Numerous spectrographic analyses confirmed the similarity of the two gold samples, and also disclosed the presence of platinum in each, this element having been overlooked in the preliminary study. It was further shown that no other gold in British Columbia carried mercury, platinum, and palladium. This evidence having been produced and accepted by the court, the defendant pleaded guilty and was duly sentenced. To the best of our knowledge this represents the first case of its kind in history, although gold from the mint has doubtless been identified by analysis on more than one occasion.

It is probable that further and more detailed work will establish the fact that gold in various camps, more rarely in individual mines, may be identified by its content of minor elements.

B. Prospecting. It is becoming more and more necessary to supplement the gold pan of the prospector with the knowledge and skill possessed by the trained geologist and mineralogist. The fact that British Columbia, before the war, produced negligible amounts of mercury and tungsten and now is capable of producing far more than is needed for the whole of Canada, is directly attributable to the knowlege and skill of trained men. It is hoped that tin, now only produced as a by-product from the Sullivan Mine, will, before long, be produced in Western Canada in important amounts. The following remarks will illustrate how the spectroscope is assisting in this search.

(1) *Tin.* Samples of placer gold from ten different localities in the Yukon Territory have been analyzed. Tin was found in gold from five of these localities, namely, Dublin Gulch, Highet Creek, Arizona Creek, Ledge Creek, and Canadian Creek. In all of these creeks, except Canadian, cassiterite can be panned and much of this cassiterite is well crystallized and is relatively little water-worn. It is, however, necessary to point out that cassiterite has been known for years to occur in various creeks in the Yukon. The surprising thing is that no systematic effort has been made to find it in place.

It is gratifying to note that systematic work is already producing encouraging results. In the summer of 1943, significant, and it is to be hoped commercial, cassiterite was found in place at Dublin Gulch.

All the stanniferous golds in the Yukon come from the Mayo District. Four of the five tin-free gold samples, namely those from Hunker, Bonanza, Klondike, and Dominion Creeks, come from the Dawson District. In the Dawson District cassiterite is found in the creeks, but it is all well water-worn and banded, differing in aspect from that found in the Mayo District. It is thought that the cassiterite in the Dawson District has been carried a considerable distance from its source. The remaining sample of placer gold which shows no tin comes from Minto Lake in the Mayo District. Interestingly enough, very little cassiterite is found in this locality, and what is found is well water-worn and has obviously been transported some distance from its source.

Gold from only one lode gold prospect in the Yukon was analyzed and this showed no tin. No tin has been recorded in this area.

The tin found in place in the Yukon and at the Sullivan is closely associated with abundant tourmaline. It seems reasonable to suggest that further search for tin be made in areas where the gold samples consistently show tin and where granitic intrusions and abundant tourmaline are known to occur.

(2) *Mercury.* Occurrences of mercury in British Columbia have long been known and there had been some production of this

metal. Recently British Columbia has become a major mercury producer.

In general the most likely places in which to prospect lie in or near areas of Tertiary vulcanism. Unfortunately, mercury tends to occur alone and consequently the gold and mercury areas do not, in general, coincide.

However, it is of interest to find that mercury is found in gold from the Mayo District, Yukon Territory, from the West Coast of Vancouver Island, and the Bridge River District. In all these areas there are occurrences of mercury at no great distance from the gold occurrence. Native silver from the Dolly Varden Mine, Portland Canal District contains mercury, and arquerite is found in Manson Creek placers, Omineca District. Thus, it is clear that mercury is widespread in the primary magmas from which many British Columbia ores were derived. Furthermore, some of the deposits in these areas are Tertiary and some Mesozoic. Consequently, it is safe to say that mercury is an important minor element in some of the British Columbia metallogenetic zones. After testing many other minerals, we have come to the conclusion that native gold and silver are the best "pathfinders" in the search for mercury. The inference is that, if gold in an area is mercury-free, there will be much less chance of finding mercury deposits than if the gold is a consistent mercury carrier.

REMARKS ON OTHER MINOR ELEMENTS.

Far too little work has been done, to draw conclusions about the occurrence of the other minor elements that have been found—namely, lead, bismuth, tellurium, arsenic, antimony, zinc, and cadmium.

In general, the minor elements found in gold may be correlated with elements in minerals known to be present in the ore. Bismuth in the Hedley and Cariboo Districts affords a good example. Conversely, there is little lead in the Dawson and Bridge River Districts and the golds from there, with only one exception, show no lead. Other examples could be cited.

TABLE II.

Note: S = Strong +0.5%
M = Medium +0.1 − 0.5%
F = Faint −0.1%.

No.	Locality.	Type of deposit.	Ag.	Cu.	Fe.	Mn.	V.	Ti.	Hg.	Pb.	Bi.	Te.	As.	Sb.	Zn.	Cd.	Sn.	Pd.	Pt.
27.	Con Mine, N. Y. T.		S	M	F				F	M	F			M	F				
28.	Elbow Lake, Manitoba	MH	M	F	F				F										
29.	Laguna, Herb Lake, Man.	M	S	F	F			F	F	S	F				M				
30.	Wekusko Lake, Manitoba	MH	M	F	F		F	F					F			F			
31.	Bruce Mines Area, Ont.	H	S	M	F			F	F	F	S	M			F				
32.	Lake Shore, Ontario	M	M	F	F	F		F	F	S		S					F		
33.	Kerr Addison, Ontario	M	S	M	F	F	F	F											
34.	Ranger Group, Van Winkle Lake, Ontario	?	S	M	F	F	F	F	F	F			F	F	F	F	F		F?
35.	Canyon Creek, Ontario	?	M	F	S	M	F	F								F	F		
36.	Lake Wanapata, Ontario	?	S	M	F	F		F	F	F							F		
37.	Hollinger, Ontario	H	S	M	F	F	F	M		F	F						F		
38.	McIntyre, Ontario	H	S	M	F	F			F	F									
39.	Raven R., Larker Lake, Ont.	M	M	F	F	F	F	F	M							F			
40.	Sullivan, Quebec	H	M	M	F	F	F	F		F		M	F	F		F			
41.	Sisco, Val D'or, Quebec	H	S	M	F														
42.	Granada, Rouyn, Quebec	M	S	F	F	F	F	F	F	F				F		F			
43.	O'Brien, Cadillac, Quebec	H	S	M	F	F		F		F				F					
44.	Maniwaki, Quebec	H	M	F	F	F		F	F		F								
45.	Belleterre, Quebec	H	S	F	F	F		F											
46.	Pandora, Que. (In greywacke)	H	S	M	F	F		F	F				F				F		
47.	Pandora, Que. (In quartz vein)	H	S	F	F	F	F	F	F	F						F			

TABLE II.—*Continued.*

No.	Locality.	Type of deposit.	Ag.	Cu.	Fe.	Mn.	V.	Ti.	Hg.	Pb.	Bi.	Te.	As.	Sb.	Zn.	Cd.	Sn.	Pd.	Pt.
48.	Ploughlead, Wine Harbour, Nova Scotia	M	M	F	F	F		F					F						
49.	Donkin Belt, Seal Harbour, Nova Scotia	M	S	M	F	F	F	F		F						F	F		
50.	Beaver Dam Mine, Sheet Harbour, Nova Scotia	M	S	M	F	F		F		F	M			F	F				
51.	Maid of Mexico, Alaska	H	S	M	F	F		F		S				F			F		
52.	McQuillan Creek, Calif.	P	S	M	F	F	F	F	F										
53.	Rochester, Nevada	H	S	M	F	F	F	F	F	F				F	F		F		
54.	Cripple Creek, Colorado	E	S	M	F	F	F	F	F	F	M	F							
55.	Brewer Mine, S. Carolina	H	S	M	F	F	F	F		F			F			F			
56.	Black Hills, S. Dakota	H	M	M	F			F							F				
57.	Clarabelle Mine, S. Dakota	H	S	M	F	F		F	F	F	S		F	F					
58.	San Mauricio, Philippines	M	S	F	F	F				F				F					
59.	Matloui, S. Rhodesia	?	S	F	F				F										
60.	Golden Valley, S. Rhodesia	?	S	M	F				F										
61.	Victoria, Australia	H	S	M	F	F	F	F	F	F	S	S							
62.	Barberton Reef, S. Africa	?	S	F	F		F	F	F										
63.	Minas Geraes, Brazil	H	S	M	S	F		F					S	S		F		F	M
64.	Boliden, Sweden	H	M	F	F					S									
65.	Verespatak, Hungary	E	S	M	F	F	F	F		F					F				
66.	Berezovsk, Russia	H	S	M	F			F	F	S	S			F					

Please see note re symbols at foot of Table I.

However, apparent exceptions should also be cited, if only to keep the record straight. Lead is found in the Cariboo Gold Quartz ores, but none in the gold from this mine. The same is true of tellurium. This element has been found in the Cariboo and Hedley Districts, but was not observed in analyses of the gold. It may be that more detailed work will eventually show up minute amounts of some of these elements which are here reported absent.

OTHER ANALYSES OF GOLD SAMPLES FROM OUTSIDE BRITISH COLUMBIA.

The above results, incomplete and inconclusive though they are, aroused our curiosity and we "shot" all the other samples of native gold available to us. Table II summarizes these results.

GENERAL CONCLUSIONS.

A glance through the above table shows that, even after taking into account the fact that some of the samples come from unknown collectors, the same general conclusions seem to hold for gold deposits in general as have been postulated as a result of the limited work done in British Columbia. These conclusions are:

(1) Metallogenetic provinces or zones are of more importance than the type of deposit in which the gold occurs in determining the minor element content of native gold.

(2) Each metallogenetic province or zone tends to show a characteristic assemblage of minor elements in gold. The absence of mercury in the gold from Nova Scotia and the absence of tin in the three samples of European gold are examples of interest, although it is possible that further work may show that these results were merely coincident.

(3) There is good reason to hope that other workers will be able to substantiate some of the above results. Our finding of platinum and palladium in the gold from Minas Geraes lends support to this hope. At the time we analyzed that sample, we

did not know that these elements had been discovered in it many years ago.[5]

However, it is hoped that this paper will stimulate other workers to carry on further and more detailed studies in this field, and that, eventually, there will be sufficient recorded facts for conclusions to be drawn which will assist those who are studying the genesis of gold in ores.

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The authors wish to acknowledge the assistance given to them by their colleagues in the Department of Geology: by their timely criticism and advice they aided greatly. Thanks are also offered to Frank Ebbutt of the Howe Sound Company: Mr. Ebbutt generously contributed from his own collection many of the samples which were used and also helped in revising the manuscript. The authors also wish to express their thanks to the many mining companies who contributed gold samples, and particularly the Granby Mining Company for permitting the publication of results obtained on their samples. Lastly, thanks are owing to the Physics Department of the University for their kindness in permitting us to use their Hilger Spectroscope.

UNIVERSITY OF BRITISH COLUMBIA,
January 31, 1944.

[5] Beyschlag, Vogt and Krusch: Ore Deposits. Trans. by S. J. Truscott. MacMillan and Company. P. 1225.

SOLUBILITY OF METAL SULPHIDES IN DILUTE VEIN FORMING SOLUTIONS.

R. M. GARRELS.

ABSTRACT.

On the basis of several widely accepted geological and chemical assumptions, the theory and method for quantitative calculation of simple metal sulphide solubilities at elevated temperatures in dilute vein solutions is presented. Quantitative solubility data for copper are calculated over a wide range of temperature, acidity, and concentrations of salts. From the calculations it is concluded that dilute acid solutions, regardless of composition or temperature, cannot carry dissolved metal sulphides. The case for alkali sulphide transport is discussed, with the conclusion that colloids must play an important part in sulphide transportation.

INTRODUCTION.

THE problem of metal sulphide transport from the magma to the final resting place in veins or other hydrothermal deposits has received a great deal of attention in the geological literature. The sulphide solubilities in pure water are vanishingly low, and geologists have been hard-pressed to find a reagent which will meet the conditions imposed by geologic relations and at the same time be powerful enough to carry enough sulphide in solution to form the tremendous deposits which are known. The complexity of vein solutions, the lack of chemical data at high temperatures and pressures, the disagreement among geologists as to the chemical conditions imposed by the field relations—all have been barriers to a quantitative solution of the problem.

However, in the last few years important data have been supplied through work by Verhoogen [1] on the solubility products of the simple sulphides; by Smith [2,3] on solubility in alkaline sulphide solutions; and by Owen and Brinkley [4] on the effect of high pressures upon ionic equilibria. These data have made a semi-quantitative treatment of the problem possible, even though a great deal of latitude must be allowed for variations in geological conditions.

ASSUMPTIONS NECESSARY FOR QUANTITATIVE SOLUBILITY CALCULATIONS.

The following assumptions were used as a basis for the solubility calculations given below:

[1] Verhoogen, Jean: Thermodynamical calculation of the solubility of some important sulphides, up to 400° C. ECON. GEOL. 33: 34–51; 775–778, 1938.

[2] Smith, F. G.: Experiments on the transportation and deposition of sulphides in alkaline sulphide solutions. M.Sc. Thesis, Univ. of Manitoba, 56 pp., 1939

[3] ——: The alkali sulphide theory of gold deposition. ECON. GEOL. 38: 561–589, 1943.

[4] Owen, B. B., and Brinkley, J. R.: Calculation of the effect of pressure upon ionic equilibrium in pure water and in salt solutions. Chem. Rev. 29: 461–474, 1941.

(1) The sulphur which precipitates the metals as sulphides is carried in solution with them, and is in the bi-valent state.

(2) No single constituent, such as chlorine, iron, or arsenic, is present in concentrations greater than 0.1 molar. This represents a maximum for any single constituent of about 10,000 parts per million of solution by weight. The total weight of all solutes may, of course, be higher, but a maximum of 20,000 parts per million total salts is assumed.

(3) The temperatures of formation of most deposits are in the range 25°–400° C.

(4) The pressures at the time of vein formation are not substantially greater than 1,000 atmospheres. This corresponds to a hydrostatic pressure at a depth of 30,000 feet, or a uniform rock pressure at 10,000 feet. Also, it is assumed that pressure is uniform, with no shear component.

(5) No nitrogen-containing complexes, such as ammonia or cyanide, are present.

It is hoped that none of these assumptions will meet serious objections. There may be special cases to which they are not applicable, but they certainly represent majority opinion concerning most vein deposits.

Particular attention is called to the fact that no restrictions are placed complexity of composition or on acidity or alkalinity, except that they fall within the concentration maximum stated.

THEORY AND METHOD FOR QUANTITATIVE SOLUBILITY CALCULATIONS.

When Verhoogen [5] presented his solubility data on the metal sulphides, he calculated the values of solubility in pure water. These values, except as sample calculations, are of little use to the geologist, for pure water is unknown in nature. However, Verhoogen also presented the *solubility product constants* of the sulphides. These constants are valid wherever chemical equilibrium obtains, even in the complex solutions which carry sulphides, sulphosalts, tellurides, and numerous gangue minerals. Since the solubility product constant will be used as the foundation of the following calculations, it may bear a geologic reframing and an analysis of its applications to vein solutions, even though a discussion of its meaning in chemical terms can be found in any elementary chemistry text.

It may be recalled that at any given temperature and pressure, a metal sulphide will precipitate from a vein solution when the product of the metal ion and sulphide ion concentrations reaches a fixed value, the solubility product constant. No limitations are placed on the concentration or complexity of components present. It is the unswerving devotion of the solubility product to its own ions and to no others which makes it applicable to vein solutions in general.

It is expedient here to frame the solubility product constant equation so that it contains a term which represents the actual solubility of any given bivalent metal and a term which represents the total bivalent sulphur

[5] Verhoogen, Jean: op. cit., pp. 34–51, 775–778.

concentration of the solution. As it is usually given, for chemical use, the constant for a bivalent metal sulphide is written:

$$(Me^{++})(S^{=}) = K \qquad (1)$$

(Me^{++}) = concentration of metal *ion* in mols per liter.
$(S^{=})$ = concentration of sulphide *ion* in mols per liter.
K = solubility product constant at the temperature and pressure of the solution.

In complex solutions at various acidities, (Me^{++}) is not equal to metal solubility, nor is $(S^{=})$ equal to the total amount of bivalent sulphur present.

The metal solubility is equal to the metal ion concentration, plus the concentrations of any other ionic species containing the metal:

$$(Me_{sol}) = (Me^{++}) + (MeCl^{+}) + (MeS_2^{=}) + \cdots$$

The total bivalent sulphur in the solution is equal to the sulphide ion concentration plus the concentrations of any other species containing bivalent sulphur:

$$(S_{sol}) = (S^{=}) + (HS^{-}) + (H_2S) + \cdots$$

Thus the metal solubility is larger than the metal ion concentration, and must be multiplied by some factor X so that an equality can be established:

$$(Me_{sol})X = (Me^{++}) \qquad (2)$$

The total sulphur concentration times some other unknown value Y is equal to the sulphide ion concentration:

$$(S_{sol})Y = (S^{=}) \qquad (3)$$

Substituting the values thus obtained for (Me^{++}) and $(S^{=})$ from equations (2) and (3) into equation (1), an equation containing both metal and sulphur total concentrations is obtained:

$$[(Me_{sol})X][(S_{sol})Y] = K \qquad (4)$$

This equation lends itself very conveniently to a discussion of the various mechanisms that have been advanced to render the metal sulphides soluble. The acid solution advocates, for instance, add excess hydrogen ion to the solution. This reacts with sulphide ion as follows:

$$H^{+} + S^{=} \rightleftharpoons HS^{-} + H^{+} \rightleftharpoons H_2S \qquad (5)$$

Thus the remaining $S^{=}$ ion forms a very small proportion of the total bivalent sulphur in solution, much of which is tied up in HS^{-} and H_2S. Consequently, the term Y in equation (4) must be a very small fraction. If Y is small enough, then the other three terms S_{sol}, Me_{sol}, and X can be correspondingly large before the K value is reached. It is clear from this

that the Y term is really a measure of the repression of the sulphide ion concentration.

The alkali sulphide school, on the other hand, rely on a diminution of the X value by repression of the metal ion concentration. They postulate the repression of the metal ion by formation of complex ions of the type MeS_n^{2n-2}:

(Other forms of the complex sulphide ion are possible, but this general form, in which the valence is equal to twice the number of sulphur atoms minus two, is the most common.)

$$Me^{++} + nS^{=} \rightleftharpoons MeS_n^{2n-2} \qquad (6)$$

In this case, the ratio of metal ion to total metal in solution becomes small, or, referring to equation (4), X becomes very small. Since X is small, then Me_{sol}, S_{sol}, and Y may be relatively large.

It is interesting to note here that the two schools of transport are mutually exclusive—that is, the alkali school maintains a large value of Y because they need the sulphide ion to force the metal into the complex metal sulphide ion according to equation (6). The acid school, on the other hand, have to tolerate a large X value because they are intent on diminishing Y by repressing the sulphide ion concentration. To increase X, Y and total sulphur must be increased.

It is obvious that the optimum condition for large metal solubility would be some type of solution which repressed both metal ion concentration and sulphide ion concentration at the same time, giving very small values of both X and Y. The total sulphur in solution can never be very low, for enough must always be present to unite with all the metals present to form the sulphides found in the veins.

Since Verhoogen has calculated the solubility product constants for simple sulphides up to 400° C., the K in equation (4) is known through the range of vein formation.

The total sulphur (S_{sol}) must be sufficient to precipitate all metals from solution, so it seems reasonable to assign a series of concentrations between 0.001 and 0.1 mols per liter as the sulphur content of the solutions. If the total sulphur were less than 0.001 mols per liter, the total metal content would also have to be of the same order of magnitude. It is difficult to ascertain what the proponents of dilute solutions mean, in terms of molar concentration, by "dilute," so the range 0.1 to 0.001 is the author's conception of the meaning of this word to other geologists. Fortunately, after the solubilities are calculated for this range of concentration, and presented in tabular form, any reader can determine solubility at any sulphide concentration which meets his own conception of "dilute," without recourse to paper and pencil.

With K and S_{sol} out of the way, the metal solubility can be determined if the X and Y values can be determined. It is not necessary to determine anything but the minimum values for X and Y, since the values to be calculated are to represent the maximum solubility of the metal in vein solutions.

The Y values are a measure of the repression of the sulphide ion according to equation (5). Verhoogen [6] has calculated the equilibrium constants for this reaction over the range 25°–400° C., so that the amount of repression of the sulphide ion can be obtained at any given acidity. The objection may be raised here that sulphur occurs not only in $S^=$, H_2S, and HS^-, but in metal-sulphur complexes as well. That is true, but since the formation of such complexes demands a relatively high concentration of $S^=$ ion, Y values cannot be low in such solutions because Y (see equation 3) is the ratio of sulphide ion to total sulphur in solution.

The X values have been studied in detail by the author.[7,8] The conclusions drawn from this work are as follows:

(1) Positive ions such as Na^+, K^+, Li^+ and others do not repress the concentration of lead, zinc, copper or other simple metal ions.

(2) Negative ions such as chlorine, fluorine, iodine, and bromine have a nearly uniform effect in concentrations up to 0.1 molar. This effect is to reduce the metal ion concentration to a minimum of 10 per cent of the total metal in solution. In other words, if mixed salts are added to a 0.1 molar solution of copper chloride, 0.01 mols of copper are in solution as Cu^{++} ion, while the other 0.09 mols are tied up in various complexes with the salts. This is the equivalent of an X value of 0.1.

(3) Sulphide ion has an effect which makes it an exception to this general salt effect. Its influence in depressing the metal ion concentration ranges from a very strong repression in the case of mercury to little or no repression in the case of iron.

X values can be determined, then, only in cases in which the repression of metal ion by sulphide ion is quantitatively known. At present data are at hand only for copper and mercury, and these two only at temperatures less than 100° C. However, since Smith [9] has established the relative effects of sulphide ion in forming complexes with the common metals, a set of quantitative solubility values calculated for copper alone gives a yardstick to which the others can be compared.

QUANTITATIVE CALCULATION OF COPPER SOLUBILITY.

Copper makes a good guinea pig for the solubility calculations, for the value of its solubility product constant lies between those of mercury and silver on one hand, and lead and zinc on the other. Also, the repression of copper ion by sulphide ion is less than the repression of mercury ion by sulphide ion, and more than the repression of lead and iron.

In a sample calculation, a hydrogen ion concentration of 0.1 normal, a total bivalent sulphur solubility of 0.1 molar, and a temperature of 25° C.

[6] Verhoogen, Jean: op. cit., p. 47.

[7] Garrels, R. M.: The Mississippi Valley type lead-zinc deposits and the problem of mineral zoning. ECON. GEOL. 36: 729–744, 1941.

[8] ——: The effect of electrolytes of the solubility of metal sulphides in vein solutions (abst.). ECON. GEOL. 36: 848, 1941.

[9] Smith, F. G.: The alkali sulphide theory of gold deposition. ECON. GEOL. 38: 569–570, 1943.

are assumed. The following equilibria necessary for the calculation are known:[10]

$$(Cu^{++})(S^{=}) = K_{CuS} = 2.3 \times 10^{-38}$$

$$\frac{(Cu^{++})(S^{=})^3}{(CuS_3^{-4})} = K_{CuS_3^{-4}} = 2.5 \times 10^{-36}$$

$$\frac{(H^{+})(S^{=})}{(HS^{-})} = K_{HS^{-}} = 1.0 \times 10^{-15}$$

$$\frac{(H^{+})(HS^{-})}{(H_2S)} = K_{H_2S} = 1.1 \times 10^{-7}$$

$$(HS^{-}) + (H_2S) + 3(CuS_3^{-4}) + (S^{=}) = 0.1$$

There are five unknowns to be determined, but also five equations which relate them, giving:

$$(Cu^{++}) = 2.3 \times 10^{-17} \text{ mols per liter.}$$

$$(CuS_3^{-4}) = 1.0 \times 10^{-48} \text{ mols per liter.}$$

$$(S^{=}) = 1.0 \times 10^{-21} \text{ mols per liter.}$$

The general equation for the solubility product (equation 4) is:

$$[(Me_{sol})X][(S_{sol})Y] = K \qquad (4)$$

Since total sulphur (S_{sol}) is 0.1 mols per liter, and ($S^{=}$) ion is 1.0×10^{-21} mols per liter:

$$Y = \frac{(S^{=})}{(S_{sol})} = \frac{1.0 \times 10^{-21}}{1.0 \times 10^{-1}} = 1.0 \times 10^{-20} \qquad (3)$$

This merely states that only $1/10^{20}$ of the total sulphur in solution is in the form of sulphide ion.

As has been shown, the X value is a measure of the repression of the metal ion concentration, and is due to the salt effect plus the complex sulphide effect. The maximum salt effect is to tie up nine-tenths of the copper in complexes with the various salts; the sulphide effect in this acid solution is to tie up 1.0×10^{-48} mols of copper in the copper-sulphur complex. So the X value is:

$$X = \frac{(Cu^{++})}{(10Cu^{++}) + (CuS_3^{-4})} = \frac{2.3 \times 10^{-17}}{2.3 \times 10^{-16} + 1.0 \times 10^{-48}} = 10^{-1} \qquad (2)$$

[10] The equilibrium constants, except for the CuS_3^{-4} value are from Verhoogan (Verhoogen, Jean, op. cit., p. 47; p. 777). The equilibrium constants for the CuS_3^{-4} complex at 25° C., 50° C., and 75° C. have been calculated by the author from data on copper solubility in Na_2S solution. (Holtje, R., and Beckert, J.: Zeit. Anorg. Allgem. Chem., vol. 142, p. 115, 1925.) These calculations are straightforward chemical manipulations, and have been checked by several persons (see *Acknowledgments*), so it was not thought necessary to include them in a geological discussion.

Or, in words, one tenth of the copper in solution is in the form of free copper ion.

Substituting in equation (4):

$$[(Cu_{sol})(10^{-1})][(10^{-1})(10^{-20})] = 2.3 \times 10^{-38}$$

Solving for (Me_{sol}):

$$(Me_{sol}) = 2.3 \times 10^{-16} \text{ mols per liter.}$$

In alkaline solutions, the formation of CuS_3^{-4} ion is more important. A brief summary of the same type of calculation at an OH^- ion concentration of 0.1 normal, other conditions the same, may illustrate the point.

Solving the same five equations, but using a pH of 13 ($OH^- = 10^{-1}$) instead of a pH of 1 ($H^+ = 10^{-1}$):

$$(S^=) = 10^{-3} \text{ mols per liter.}$$

$$(CuS_3^{-4}) = 9 \times 10^{-8} \text{ mols per liter.}$$

$$(Cu^{++}) = 2.3 \times 10^{-35} \text{ mols per liter.}$$

Then

$$Y = \frac{(S^=)}{(S_{sol})} = \frac{(10^{-3})}{(10^{-1})} = 10^{-2}$$

and

$$X = \frac{(Cu^{++})}{(10Cu^{++}) + (CuS_3^{-4})} = \frac{2.3 \times 10^{-35}}{2.3 \times 10^{-34} + 9 \times 10^{-8}} = 2.5 \times 10^{-28}$$

Substituting again in equation (4) the values of X, Y, S_{sol}, and K:

$$[(Cu_{sol})(2.5 \times 10^{-28})][(10^{-1})(10^{-2})] = 2.3 \times 10^{-38}$$

$$Cu_{sol} = 9 \times 10^{-8} \text{ mols per liter.}$$

A table of values is given below which shows solubilities at various assumed values of acidity, alkalinity, total sulphur, and temperature.

DISCUSSION.

It may be worthwhile to discuss the validity of the values before drawing any conclusions from them. The best way, perhaps, is to anticipate objections which may arise.

The effect of pressure has not been discussed. The data of Owen and Brinkley [11] show that this neglect is justified. The effect of uniform pressure on ionic equilibria is approximately the same in pure water as in salt solutions, and has the effect of multiplying the equilibrium constant for any given reaction by a factor of 3 to 8 at a pressure of 1,000 atmospheres. This increases the solubility product constant by this relatively negligible

[11] Owen, B. B., and Brinkley, J. R.: Calculation of the effect of pressure upon ionic equilibrium in pure water and in salt solutions. Chem. Rev. 29: 461–474, 1941.

amount, and at the same time it increases the ionization of the complexes which repress the metal and sulphide ions, the net effect upon solubility being practically zero. In any case, a factor of 3, 8, or even 100 would not effect the order of magnitude of the solubility values.

TABLE I.

SOLUBILITY OF COPPER IN SULPHUR BEARING SOLUTIONS.

(mols per liter)

Total S in Solution	pH Values						
	1	3	5	7	9	11	13
Copper in Mols Per Liter of Vein Solution.							
A. 25° C.							
0.1 mol/liter	2.3×10^{-16}	2.3×10^{-20}	2.3×10^{-24}	3.5×10^{-19}	9.0×10^{-16}	9.0×10^{-12}	9.0×10^{-8}
0.01 mol/liter	2.3×10^{-15}	2.3×10^{-19}	2.3×10^{-23}	3.5×10^{-21}	9.0×10^{-18}	9.0×10^{-14}	9.0×10^{-10}
0.001 mol/liter	2.3×10^{-14}	2.3×10^{-18}	2.3×10^{-22}	3.5×10^{-23}	9.0×10^{-20}	9.0×10^{-16}	9.0×10^{-12}
B. 50° C.							
0.1 mol/liter	1.8×10^{-16}	1.8×10^{-20}	1.8×10^{-24}	1.6×10^{-18}	3.6×10^{-15}	3.6×10^{-11}	3.6×10^{-7}
0.01 mol/liter	1.8×10^{-15}	1.8×10^{-19}	1.8×10^{-23}	1.6×10^{-20}	3.6×10^{-17}	3.6×10^{-13}	3.6×10^{-9}
0.001 mol/liter	1.8×10^{-14}	1.8×10^{-18}	1.8×10^{-22}	1.6×10^{-22}	3.6×10^{-19}	3.6×10^{-15}	3.6×10^{-11}
C. 75° C.							
0.1 mol/liter	2.0×10^{-16}	2.0×10^{-20}	2.0×10^{-24}	6.0×10^{-18}	1.0×10^{-14}	1.0×10^{-10}	1.0×10^{-6}
0.01 mol/liter	2.0×10^{-15}	2.0×10^{-19}	2.0×10^{-23}	6.0×10^{-20}	1.0×10^{-16}	1.0×10^{-12}	1.0×10^{-8}
0.001 mol/liter	2.0×10^{-14}	2.0×10^{-18}	2.0×10^{-22}	6.0×10^{-22}	1.0×10^{-18}	1.0×10^{-14}	1.0×10^{-10}
D. 200° C.							
0.1 mol/liter	8.8×10^{-15}	8.8×10^{-19}	8.8×10^{-23}				
0.01 mol/liter	8.8×10^{-14}	8.8×10^{-18}	8.8×10^{-22}				
0.001 mol/liter	8.8×10^{-13}	8.8×10^{-17}	8.8×10^{-21}				
E. 400° C.							
0.1 mol/liter	4.4×10^{-13}	4.4×10^{-17}	4.4×10^{-21}				
0.01 mol/liter	4.4×10^{-12}	4.4×10^{-16}	4.4×10^{-20}				
0.001 mol/liter	4.4×10^{-11}	4.4×10^{-15}	4.4×10^{-19}				

It may be argued that copper can be carried in the cuprous rather than the cupric state. Verhoogen's data [12] show that the solubility product of cuprous sulphide is of the same order of magnitude as that of cupric sulphide. A calculation similar to that for cupric sulphide shows that at a temperature of 400° C., total sulphur 0.1 mols per liter, and acidity 0.1 mols per liter, cuprous sulphide is soluble to the extent of 8.0×10^{-10} mols per liter.

[12] Verhoogen, Jean: op. cit., p. 775.

Also, it may appear that the argument is directed only toward the single mineral covellite, and that copper may be carried as chalcopyrite, or as sulphosalts. The calculations merely give the amount of copper which can exist in solution before covellite will precipitate. Other minerals may precipitate before covellite, but only if they are less soluble. If the amount of copper in the solution exceeds the amount given in the table, precipitation will occur.

Finally, the objection that some effect of the multiplicity of ions in solution has been overlooked. It is a philosophical possibility, but neither the thermodynamic work by the author on salt effect, his calculations from other thermodynamic data, nor the material on copper from a good text on qualitative analysis [13] gives any clue that any substances which might cause repression of sulphide or metal ion concentration were overlooked. The burden is certainly upon the objector now to suggest some new mechanism, rather than to appeal blandly to complex solutions.

Acid Solutions. The values in the table for acid solutions are complete up to 400° C. The effectiveness of dilute acid solutions, even at high temperatures, may be illustrated as follows. If a cube two-thirds of a mile on a side were filled with a solution carrying 0.1 mol of bivalent sulphur per liter, and 0.1 normal in acid at 400° C., not more than 1 mol of copper (64 grams) could be dissolved before precipitation would occur. Or, to put this illustration as a dynamic, rather than as a static picture, a volume of dilute solution equal to that of the Mediterranean sea must have passed between the walls of every vein which contains a few tons of copper ore.

Acid solutions can be effective as metal carriers only if the acid is present in very high concentrations. *Dilute and weakly acid solutions are not capable of carrying metals.*

Alkaline Solutions. It is immediately obvious from the lack of information on the copper-sulphur complex above 75° C. that no quantitative deductions can be made about copper solubility in the ore-forming range of temperatures in alkaline solution. However, the form of the complex has been determined, and the road is open to theoretical treatment when solubility data at higher temperatures are available. Also, it is clear that copper solubility goes through a minimum approximately at the neutral point.

Smith is the strongest proponent of alkali sulphide solutions as the ore-bearing medium.[14] It is the opinion of the author that such solutions truly represent the method of synthesis and collection of metal sulphides from the magma, but that there are a number of chemical and geological limitations on effective transportation of the metal sulphides *dissolved* in such solutions.

First, Smith admits that iron does not form sulphur complexes in aqueous solution even at elevated temperatures,[15] and is soluble only to a

[13] Reedy, J. H.: Theoretical Qualitative Analysis. McGraw-Hill Book Co., New York and London, 1938. Pp. 199–204.

[14] Smith, F. G.: The alkali sulphide theory of gold deposition. ECON. GEOL. 38: 561–590. 1943.

[15] Op. cit., pp. 569–570.

very limited extent in sodium sulphide *melts*. This means that alkali sulphide solutions are incapable of carrying more than minute quantities of iron, even under hypothermal conditions. Smith apparently avoids this difficulty by producing pyrite by reaction of the sulphides with iron bearing wall rock.[16] There are many veins, however, which have pyrite in the central zone, showing clear evidence of transportation. There are, of course, many other cases in which iron shows clear evidence of movement, and alkali sulphide solutions are incapable of transporting iron *in solution*.

Second, the alkali sulphide theory has yet to demonstrate that it can be put on a quantitative as well as a qualitative basis. The experiments carried on so far are more accurately described as work with fusions rather than with anything corresponding to vein solutions. The case of acid solutions illustrates that the problem is quantitative and not qualitative in nature. Very concentrated acids dissolve sulphides, weak acids are entirely ineffective. Concentrated alkali sulphide solutions will dissolve most metal sulphides, but what of dilute alkali sulphide solutions?

Alternatives. There are, at present, no alternatives to acid or alkali sulphides. The prerequisites for an effective metal transporting medium are, fortunately for geologists, very stringent. The medium must contain substances which will depress, with great effectiveness, either the sulphide ion concentration, or the concentration of all metal ions. No hint of such universal depressants, outside of acid or alkali sulphide, has ever appeared in the chemical or geological literature, and it is fairly safe to say that the answer to the problem of metal sulphide transport in solution lies in the realm of one of these two schools of thought. Either one of them holds the answer, or the sulphides are not transported in the dissolved state.

General Objections To Transportation In Solution. There is one aspect of mineral relations in veins which suggests very strongly that the method of transportation of the metal sulphides is in a dispersed solid phase, or at least not in solution. The minerals which are late, paragenetically, are the ones which are carried farthest from the source magma. In the case of galena and sphalerite, for instance, this may be interpreted as follows: As the lead and zinc move up the fissures, zinc deposits first, while lead is carried farther before deposition. As time goes on, and the solutions become cooler, the lead deposition takes place where zinc deposition was going on before, and the lead is found interior to the zinc in the vein. The inference is clear that the lead was more soluble than the zinc in the vein solution. However, lead (galena) very often partially replaces zinc (sphalerite). This relation is true for the sulphides in general—the mineral which is later paragenetically replaces its predecessor. Indeed, it is one of the bases on which paragenetic relations are established microscopically. There is, of course, a great deal of individual variation among deposits but the generalization that the interior minerals in veins extend closer to the surface, or farther from the source, is well established.

This gives rise to a paradox. If the interior minerals travel farther, they must be more soluble than the exterior ones, and yet they must be

[16] Op. cit., p. 583.

less soluble, because they replace the exterior minerals. Either replacement is not a criterion of solubility, or distance of transport is not. If the successive deposition of minerals depends upon the order of their solubility, then each successive mineral should merely encrust its predecessor, never replace it. As an example, if a solution of copper chloride and sodium chloride is allowed to evaporate, copper chloride crystallized first, then an intergrowth of sodium and copper chlorides, then an incrustation of sodium chloride. Sodium chloride does not replace copper chloride. When galena replaces sphalerite, lead is substituted for zinc in the sulphide, because the lead has a greater tendency to come out of solution than zinc, or, conversely, zinc has a greater solution pressure.

It seems probable that the answer is that transportation is not a solution phenomenon except in part, and that the dominant role is played by a colloidal phase.

The case for colloids has been argued authoritatively by Lindgren [17] and Boydell.[18] It is not within the scope of this paper or the author's abilities to reopen the case, except to emphasize a few points. (1) A highly dispersed solid phase is in equilibrium with its saturated solution, and so has all the chemical advantages of a saturated solution, plus a reservoir of depositable material in the solid form. It has been argued, for instance, that a dispersed galena sol could not penetrate fine grained wall rocks to form replacement deposits. If the sol were moving in a trunk fissure, its saturated solution would penetrate the wall rock, cool, and precipitate galena. This would establish a precipitation gradient, with the sol in the trunk fissure continuously dissolving and migrating outward to form the replacement deposit in the wall rock. The final deposit would give no clue to the colloidal stage in its origin. Moreover, such a mechanism would allow the metals to be transported as sols, and be precipitated chemically, rather than coagulated, so that in most cases true chemical replacement relations would be observed.

(2) Smith's method of synthesis of the sulphides at depth, then precipitation as a highly dispersed sol, transportation as a sol, and eventual deposition in crystalline form as the peptizing agent (H_2S?) is dissipated might shed new light on the mineral zoning problem, the metasomatic replacement problem, and the problem of rich deposits in solution traps.

Summary and conclusion.

(1) The theory and method for quantitative calculations of sulphide solubilities in complex dilute vein solutions is presented.

(2) The solubility of copper in dilute acid vein solutions is calculated up to 400° C.

(3) The solubility of copper in dilute alkali sulphide solutions is calculated up to 75° C.

[17] Lindgren, Waldemar: Succession of minerals and temperatures of formation in ore deposits of magnetic affiliations. A. I. M. E. Tech. Pub. 713, 23 pp., 1936.

[18] Boydell, H. C.: A discussion on metasomatism and the linear "force of growing crystals." Econ. Geol. 21: 1–56, 1926.

(4) Copper is carried in dilute alkaline solutions in the complex CuS_3^{-4}.

(5) The conclusion is reached that dilute and weakly acid solutions (less than 0.1 normal in acid, 0.1 molar in any given salt, or 0.2 molar in total salts) are incapable of carrying metal sulphides in solution.

(6) The problem of alkali sulphide transport is discussed qualitatively. The chief objection raised is the inability of such solutions to carry iron.

(7) Geological and chemical evidence is cited to show that transportation of the metal sulphides is probably in a dispersed solid state.

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NORTHWESTERN UNIVERSITY,
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PETROGRAPHIC ANALYSIS BY FRAGMENT COUNTING.[1]

FELIX CHAYES.[2]

ABSTRACT.

The applicability of normal frequency distribution to errors in petrographic analysis by grain count is now generally assumed. In this paper it is shown that for the particular counting method described the error of the count is considerably smaller than would be predicted from normal distribution. From experimental data an equation exhibiting counting error as a function of the number of grains counted and the composition-level is developed; these relations are also presented graphically. It is suggested that, regardless of the distribution of counting error, the length of count can affect only the counting error proper. Empirical equations developed in this paper apply only to the error of counting, and take no account of variations in grain-size, grain-shape, specific gravity, and systematic or erratic errors in sampling. A study of micro-sampling is now in progress and other analytical factors will be investigated later. With a counting method of known error as a base, experimental evaluation of other laboratory errors should be relatively simple.

I. THE COUNTING ERROR.

THE use of the microscope in conjunction with ore-dressing studies and operations has been commonplace since before the first World War. Determinations of particle size, degree of liberation, etc., led naturally to rapid, if somewhat crude, estimates of composition based on volume, areal, linear, or number frequency. Because of the speed with which most metallic minerals could be analyzed chemically, there was no demand for more than qualitative or, at best, semi-quantitative analytical microscopy. The application of froth flotation, agglomerate tabling, and the varied retinue of beneficiation techniques to the non-metallic or "industrial" minerals created very serious difficulty in the matter of chemical analytical control, since analyses of most of these minerals are difficult and time-consuming.

It was inevitable that any widespread development of research concerned with beneficiation of the industrial minerals would be accompanied by a demand for a more rapid method of control analysis. It was almost inevitable that some form of microscopic frequency measurement would be pressed into service to meet this demand, for the microscope was already in use in the mineral-dressing laboratory; microscopic technique required neither the fine-grinding nor fusing of chemical analysis; and microscopic analysis, if feasible at all, would be rapid.

In mineral dressing the mode, or actual content of minerals, establishes a limit to the effectiveness of mechanical beneficiation. A modal separation is

[1] Published by permission of the Director, Bureau of Mines, U. S. Dept. of the Interior.
[2] Petrographer, Eastern Experiment Station, Bureau of Mines.

a perfect separation, even if the results, in terms of the chemical composition of the products, are unsatisfactory. In sharp contrast to chemical analysis, petrographic analysis is modal. To the mineral technologist this is an advantage that may be slight, as when, in a typical beryl pegmatite, all of the desired element occurs in only one mineral; considerable if the desired element is present in more than one mineral but absent from the gangue, as in a spodumene-amblygonite pegmatite from which a lithium concentrate is to be extracted; or critical if the desired elements are present in both ore and gangue minerals, as in an andalusite or sillimanite schist from which either of these minerals is to be removed. In this last case, for instance, full chemical analyses, including tests for several elements that should be absent from the concentrate, may be required even in routine analytical control work. If the composition of each mineral present in the ore is known, it is possible in some cases to approximate the mode by computation, but even the best approximation will be subject to large errors stemming from minor (and often permissible) variations in analytical values for non-essential elements. The superiority of a standardized fragment-analysis technique over chemical analysis in problems of this type is clear.

A program of research on the beneficiation of industrial minerals, initiated early in the last decade, has long been one of the primary concerns of the Bureau of Mines, and the development of this program has been paralleled and materially assisted by the development of petrographic analysis. From a modest beginning, petrographic control has expanded until, at the present writing, approximately 90 per cent of the products prepared by the mineral-dressing unit of the Eastern Experiment Station are analyzed by this method.

Here, as in most other mineral-dressing laboratories, fragment counts are used in the initial stages of most beneficiation experiments, and as a means of determining when the experimentation has advanced to the stage at which chemical analyses of the products are warranted. When the war program of the Bureau of Mines produced a demand for analyses far beyond the capacity of the analytical laboratory, it became necessary to effect a partial substitution of petrographic for chemical analysis. This substitution took place during the most pressing period of the mineral crisis, when there was no opportunity for a complete study of the method. Recipients of petrographic analyses were provided with full information concerning the methods used, but it soon became apparent that this was not an adequate substitute for a sound and thorough evaluation of the method. For that reason the present investigation was initiated; although it is by no means complete, results already available indicate that the method is considerably better than had been expected.

Previous Studies.

The innumerable quantitative and semi-quantitative applications of the microscope are thoroughly reviewed by Chamot and Mason (1),* who provide an excellent bibliography, as well as abstracts of many papers. Our only interest in these earlier studies will be to summarize what information they

* References are listed by number at end of paper.

contain relevant to the immediate problem—the counting error of petrographic analysis. In general, we shall want to know what count-length was considered necessary, what precision or accuracy was claimed for the result, and why. In many cases count-length is not specified, and in most of the remainder no reason is given for the value finally selected. With regard to precision, the principal clue is usually a comparison of duplicate analyses in the few cases in which these are recorded; for the rest, the only index of precision (or accuracy) is the number of significant figures included in the results, and, in some cases, no results are recorded.

The earliest industrial application of index oils as a means of differentiating quantitatively between transparent minerals seems to be due to McCaughey (2), who in 1913 described a technique for estimating the quartz content of commercial feldspar. His results were obtained by "taking the average of a series of counts, in no case, however, using sections carrying less than 75 grains." His use of the term "series of counts" is not clear, and whether "section" refers to a microscopic field or an entire mount is also unclear. He says only that the method yields an "approximate percentage."

In 1915, in a note suggesting the use of a mechanical stage and the current method of counting by intersection, D. P. Hynes (3) says that "counting should cover a sufficiently large number of grains to make the error of observation reasonably small." Regarding precision, the author says merely that the method yields "very useful information."

That precision is sometimes unnecessary in work of this type is demonstrated in a paper by K. Thomas and F. W. Apgar (4), published in 1918. In the procedure recommended by these authors the material is not sized, low magnifications are used, size corrections are estimated visually, and in all published data a count-length of 200 grains or less is indicated. The total population of five to ten fields of a given slide forms the data, or "three or four slides may be prepared . . . and two or three counts made on each." The results are quoted with two significant figures for constituents forming more than 10 per cent of the sample, almost certainly an overstatement. Apparently not much above the category of a shrewd guess, their results nevertheless serve as a guide to insure that "large-scale mill operation may be instituted along most promising lines, avoiding the chance of any radical later rearrangement of plant. . . ."

In 1918, a brief notice by C. Y. Clayton (5) claimed that 80 per cent of the chemical analyses then required in an ore-dressing study could be eliminated by the use of the binocular microscope. He concludes that "this work is only as accurate as the operator makes it, the degree of accuracy, of course, being limited. . . ." No experimental results are given, and the description specifies neither count-length nor expected accuracy.

A year later Coghill and Bonardi (6) described a method "limited in its application to those ores in which the unpolished mineral grains may be identified at sight." Sized fragments are spread on a ruled tray, and two hundred to five hundred grains are counted. The results are quoted to tenths of a per cent.

The earliest clear statement of the conditions requisite to satisfactory frequency analysis is apparently that of Schneiderhöhn (7), who in 1922 cited the following: a "satisfactorily large" number of grains must be counted, the sample must be representative, all grains must be unlocked, all grains must be of like size. For correlation of frequency and weight compositions, the specific gravity and chemical composition of the pure minerals contained in the mixture must be known. A splitter is used to obtain "a few grams" of the product, and numerous small samples are taken from this or the entire final cut is spread out on a ruled grid. The total populations of a large number of fields are recorded and averaged. In the example cited, 2,600 grains are counted, and the results are reported to tenths of a per cent. No data on precision are given, and the difference between the composition computed from the count and that given by the known weight distribution of the standard indicates that the use of three significant figures is not warranted.

In 1923, E. S. Larsen (8) suggested the use of grain counts in the examination of raw and calcined gypsum. No count-length is specified, and the method is said to have a relative accuracy of 10 per cent for composition levels between 5 and 10 per cent. Several counts were to be made and an average taken. Larsen considered grain counting less accurate than heavy-liquid separations.

Three years later H. F. Gardner (9) maintained that Larsen's method ". . . cannot be employed with certainty for quantitative determinations," but still felt that an "accuracy of 5 per cent" could be obtained on either sized or unsized material. His paper contains an early statement of what is still the major problem of petrographic analysis; the petrographer, he concludes, should ". . . determine some method of sampling so that the test sample would represent the entire sample and still be of such a size that an accurate count upon it could be made."

McCaughey's original technique was extended and refined by H. I. Insley (10) in 1927. In Insley's method an analysis consists of total-population counts of two fields in each of three mounts. The number of grains tallied apparently varies between 450 and 900, and results are quoted to a tenth of a per cent. Insley's results indicate that in quartz-feldspar mixtures the mode (or actual mineral content), as determined by fragment counting, will differ considerably from the norm, the "mineral content" computed from chemical analysis by the use of theoretical mineral molecules. The significance of this discrepancy, which hinges on the precision and accuracy of both methods, is not disclosed.*

During the past 15 years a considerable literature of quantitative ore microscopy has developed, much of it the work of R. E. Head (11) and his associates at the Intermountain Station of the Bureau of Mines. This material is exclusively utilitarian, and provides little data for an evaluation of method. Vast numbers of grains are counted, but duplicate analyses are rarely recorded. It is quite likely that the precision of many of these studies is high; the results would generally be usable even if they were not very precise and there seems

* For minerals as complex as the alkali-feldspars, close agreement between norm and mode may almost be considered as *prima facie* evidence of the inaccuracy of the microscopic analysis.

to have been no demand for a systematic quantification of the procedure. Three of the best examples of this work are cited in the bibliography.

In 1930 E. Thomson (12) reported number-counts on synthetic pyrite-magnetite mixtures, in connection with his modification of areal measurement procedure. Count-lengths are not specified, and precision is given only by an average deviation of 1.5 per cent and a maximum of 4.2 per cent. Whether these are deviations from the "known" composition of the standard or from the mean of several analyses of the sample is not clear. Because the several optical methods used by him yield more consistent results than the comparative chemical-optical-heavy liquid study of Johannssen, he comes to the surprising conclusion that "the new methods . . . are more accurate. . . ."

In 1931 Wildman (13) and Dryden (14), working independently, suggested the application of the probable error of normal distribution to fragment or particle counting. Wildman's thesis was well substantiated by a series of short counts (25 to 200 grains) on mixtures of lycopodium spores and starch grains, and the significance of his results will be apparent in the present discussion of the relation between count-length and precision of count. Dryden, on the other hand, gave no experimental data, and abundant reason for doubting the applicability of normal frequency in determining the relation of counting error to count-length will be described in this paper. That sampling error is normally distributed is possible, and it may be that total laboratory error is normal, or nearly so, but unless the total population of the mount is counted, it is difficult to see how the number of grains counted can be used directly as an index of the error of any process other than the actual count.

Analyses based on linear traverses of 5,100 grain-diameters and quoted to hundredths of a per cent were published by Thackwell (15) in 1933. For at least some percentage levels this is probably permissible, but the article offers no reasons either for count-length or stated accuracy.

An ingenious device was described by Glagolev (16) in 1934. Glagolev's counter is designed to effect an automatic, uniform lateral translation after each tally. Like Dryden and Wildman, he assumes a normal error distribution, and apparently he feels that the procedure can be applied either to thin sections or fragments. He suggests a count-length of 1,000 to 1,500 points, and a single analysis "does not require more than 20 or 30 minutes," which is a little longer than is required for a five-constituent 1,000-grain count using separately operated mechanical stage and counter. Statistically, Glagolev's procedure is very similar to that described in this paper, and for the limiting case in which the lateral traversing unit is equal to the distance between grains the methods are identical. His analysis of the problem, however, is very different from that presented here.

The 1936–37 report of the Committee on Accessory Minerals, National Research Council (17), contained valuable articles on the error and accuracy of the various "accessory" mineral separation methods used by geologists. Many of the data consist of frequency counts made on residues extracted by different methods from identical head samples. No analytical statement for error of any type is presented, and, to the extent that the results depend on frequency measurements, no such statement would be possible without prior analysis of

counting and micro-sampling error. In accordance with the suggestion of Dryden, one of the authors (Grout) assumed that counting error is normal in distribution.

In 1940 the petrographic methods of the Southern and Eastern Experiment Stations of the Bureau of Mines were described by Faust and Gabriel (18). Here, as elsewhere, the orientation has been toward the immediately practical, and since the results were satisfactory, there was no need for evaluation of the method. In their discussion of counting no sampling method is specified. Results are quoted to tenths of a per cent for count-lengths of 900 to 1,000 grains. Accuracy is indicated by close agreement of norm and mode, of which several examples are cited.

In 1942 a study of feldspar in the sands of Illinois was published by H. B. Willman (19). Willman obtained his samples by means of a microsplitter, mounted them in balsam, stained or etched the mounts, and made his counts under a binocular microscope. "Using a magnification that covered a field containing 25 to 50 grains, all the grains of each mineral in the field were counted. Usually a row of adjacent fields completely across the slide, sometimes several rows, were counted, or until 500 to 1,000 grains were counted." Neither the grain size nor the average weight of the sample is given, so it is difficult to compare the procedure with that described in this paper. In any case, Willman quotes results only to one per cent of the total, which is probably justifiable.

Faust (20) has recently described an indirect but simple method for the differentiation of magnesite from dolomite, in which grain-counts are made on the friable calcined product. Neither counting nor sampling procedures are described in detail, but results correlate well with chemical data. Faust uses Dryden's analysis of counting error in determining count-length.

During the past ten years fragment-counting has grown in popularity, but despite the manifold increase in analyses and analysts, there has been no fundamental advance in either theory or technique. In much industrial work a quick first approximation is far more valuable than a refined but tardy analysis. It is pleasant and may be useful to know that a method is potentially very good; in practice it is much more important to know just how bad it is. That most of the analyses are "good enough" is obvious, since the complaints are few. Probably because the general procedure is potentially quite precise, and because the standards by which analytical microscopy is judged are usually rather low, no thorough experimental treatment of the accuracy and precision of petrographic analysis by grain-counting is available. The present paper is offered as a first step along one of several possible paths toward a systematic quantification of fragment analysis.

Experimental Procedure and Accumulation of Data.

The general procedure of petrographic analysis by grain-count divides itself naturally into three stages:

(*a*) Collection of the original bulk sample, together with grinding and preliminary size reduction.

(*b*) Final or micro-sampling, by which a few grams or a few hundred grams are reduced to a few milligrams, mounted and prepared for the count.

(*c*) Determination of the composition of the micro-sample.

Each of these steps is subject to specific types of error, and there is no reason to believe that a formulation of the variation encountered in one step will be directly applicable to either of the other two. Nor will elimination of error in one step have any effect on errors in other steps.

With the first step the industrial petrographer is rarely concerned. His field samples are taken for him, and the ultimate interest of those who provide him with most of his raw material is not the modal composition of the earth but the modal composition of the mill feed or of some specific mill product.

The second step, in which the final, small macro-sample is reduced to a suitable micro-sample, may be accomplished by a number of different methods. (For statistical purposes it may be divided into two or more substeps.) The proper evaluation of these methods is accomplished most directly by microscopic analysis of the final product.

The third step, the determination of the composition of the micro-sample, is therefore the critical stage in the performance. With a knowledge of the variability due to the count, we can easily secure the same information with regard to the final sampling. We are then in a position to make and evaluate any improvements that seem desirable or possible in the sampling technique. (The counting technique, of course, can be varied and studied without reference to other steps in the process.)

By working on sized products, with standards made up by weight percentage, we can secure a direct correlation of number to weight per cent. This permits us to determine whether to apply specific gravity corrections in analyses of minor constituents and provides also a novel but promising approach to the study of shape factor and the more general questions of the nature of mineral fracture and the effect of grinding.

Without a standard counting method of known variance we can neither gauge nor improve the end-stage sampling. Without standard counting and sampling methods of known variance the correlation between number and weight data cannot be made to yield the information it contains about shape factor and the legitimacy of specific gravity corrections.

The present report is concerned exclusively with an evaluation of counting error. Since the error is characteristic of the specific counting technique used, it is necessary to describe the method. Results of experimental counts are then given in tabular form and the variation of "precision" or absolute error with percentage of desired constituent is shown to be parabolic, or nearly so. Equations expressing the relation for count-lengths of 100, 1,000, and 2,000 grains are developed from the experimental data, and from these a single master-equation, including count-length, percentage of desired constituent and precision-error, is derived, providing a direct analogy with the treatment of precision or "reproducibility" in analytical chemistry. This is readily converted to a form in which the relative error is a function of the number of grains counted and the percentage of desired constituent, permitting experi-

mental development analogous to the treatment of accuracy in analytical chemistry.

The analysis of a micro-sample by frequency measurement—whether of number, line or area—is itself a sampling procedure. The precision of a number count is a function of the areal distribution of the grains counted and of the ratio of the number of grains counted to the total population of the slide. The homogeneity of the slide can scarcely be measured in each analysis, and no rapid, accurate method for determining the number of grains in a slide has yet been developed. Only those counting methods which reduce to a minimum errors due to these factors should be used.

Theoretically, the counting error is reduced to zero if all the grains in the slide are counted. Except with small samples composed of large grains, however, a complete count is impractical and often inaccurate. Even ignoring the uncertainty involved in counting all grains, the reduction of a fine-grained sample to the size at which a complete count becomes practical introduces an unknown but probably large sampling error. Rough measurements indicate that 8 milligrams of 100–200 mesh sand of 2.7 average specific gravity contain between 11,000 and 16,000 grains. Even if less than 8 milligrams could be satisfactorily manipulated, it is obvious that a few more splits would introduce possibilities of considerable error in the sampling of minor constituents. These errors cannot be eliminated by extension of the count. Only where it is virtually unavoidable, that is, in the analysis of + 65-mesh sands, is total counting to be preferred.

The method generally used at the Eastern Experiment Station of the Bureau of Mines—and probably the most widely used elsewhere, as well—is the systematic counting of all grains cut by the cross-hair intersection, the lateral traverses being made at regular intervals. The width of the interval between traverses is varied inversely with the total number of grains to be counted (referred to below as count-length). The regularity of the interval and its width are designed to insure the selection of a representative assortment of grains from the slide. Ideally, the entire slide should be traversed; practically, this is necessary only when segregation is obvious prior to the count, and in such cases it is usually better to cut a new micro-sample. A sampling of at least one-half the slide area is to be preferred. For an 8-milligram sample of 100–200 mesh sand mounted under an 18 mm. cover-slip, a 1,000-grain count with traversing interval of 1 mm. usually covers about two-thirds of the slide. The grains are tabulated on a Clay-Adams integrating counter with automatic totalizer. A two-constituent count of 1,000 grains requires about 8 minutes. Additional constituents slow the count considerably, but with practice, a five-constituent count of this length can be run in 15 minutes.

For the data upon which this report is based, carefully sorted, ground and sized beryl, feldspar and fluorite were combined by weight, one series containing mixtures of beryl and feldspar, the other of beryl and fluorite. For these mixtures the 100- to 200-mesh fraction of each standard was used. The beryl-feldspar counts were run by index-difference, the samples being immersed in an oil of 1.558 refractive index. The beryl-fluorspar counts were run between crossed nicols, with the polarizing prism rotated a few degrees, aniso-

tropic grains being recorded as beryl, isotropic grains as fluorite. It happens that the coincidence or correlation between weight percentage and number frequency was very close, but for present purposes this is of no consequence.

Analyses were run on each of nine samples, ranging in beryl content from 0.9 per cent (by number) to 31.6 per cent, and, conversely, carrying between 68.4 and 99.1 per cent of fluorspar or feldspar. Each mount was subjected to ten 1,000-grain counts. The traversing sequence was varied and staggered to include as many different grains as possible in each group of 10 counts. It was also standardized, so that any error that might have been introduced by its erratic variation was held to a minimum; it is felt that the only significant experimental variable was the composition of the slide from which each successive count-group was obtained.

Precision and "Precision Error."

Table 1, below, gives the results of the experimental counts. The "per cent of constituent" is in each case the mean of ten counts on the same slide, a

TABLE 1.

Per Cent of Constituent	Probable Error (Grains per thousand)	Precision or Precision Error of Analysis †
0.9	1.39	0.1
2.0	1.82	0.2
2.2	1.58	0.2
4.0	1.88	0.2
4.1	2.12	0.2
4.8	2.14	0.2
8.5	2.48	0.2
9.1	2.18	0.2
17.5	3.04	0.3
19.0	3.31	0.3
31.6	3.83	0.4

† The ± sign is to be inferred before all statements of precision, accuracy, or probable error in this paper.

number frequency. The "error" is the probable error in grains, figured from the same group;* the "precision" is the probable error as a per cent of the total, in this case the probable error multiplied by $\frac{100}{1,000}$. Since we cannot state an error in terms smaller than the smallest unit of measurement, the minimum error for a 1,000-grain count is 1 grain, and the maximum precision of a single random 1,000-grain count is ± 0.1 per cent. The minimum difference between errors is also 1 grain.

A duplicate value for percentages in excess of 50 can be obtained by subtracting each of the figures in column 1 from 100. From the way in which the data were obtained, it is clear that the error will be symmetrically distributed about a maximum at 50. An error of 1.82 grains incurred in securing a result of 2.2 per cent beryl is also an error of 1.82 grains in securing the converse result of 97.8 per cent fluorite or feldspar.

* Probable error = (.6745) (the square root of the mean of the square of the deviations).

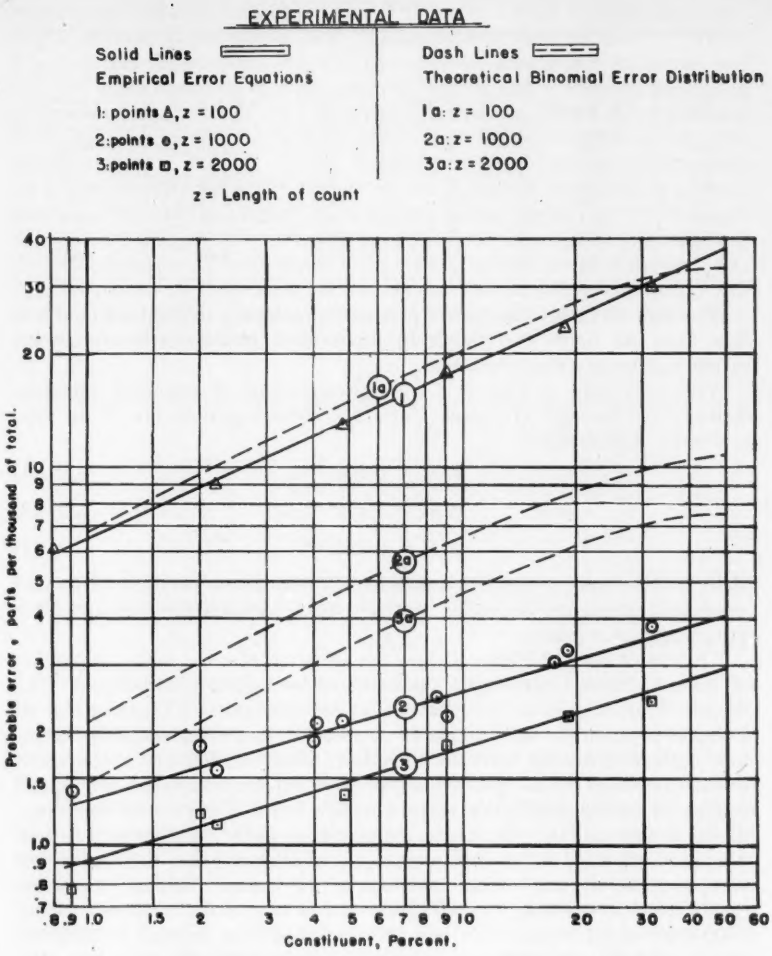

EXPERIMENTAL DATA
Solid Lines
Empirical Error Equations
1: points Δ, z = 100
2: points o, z = 1000
3: points □, z = 2000
Dash Lines
Theoretical Binomial Error Distribution
1a: z = 100
2a: z = 1000
3a: z = 2000
z = Length of count
Probable error, parts per thousand of total.
Constituent, Percent.

Figure 1—GRAPHS OF THEORETICAL AND EMPIRICAL ERROR.

Table 2 contains the same information for count-lengths (z) of 100 and 2,000 grains. The members of an original group of ten 1,000-grain counts were combined in all possible sets of two, to give the equivalent of forty-five 2,000-grain counts. Cumulative totals had been read at 100-grain intervals during the experimental counting; the counts were differenced, each group of ten 1,000-grain counts yielding the equivalent of one hundred 100-grain counts.

TABLE 2.

$z = 100$			$z = 2{,}000$		
% const.	P.E. in grains	P.E., parts per thousand	% const.	P.E. in grains	P.E., parts per thousand
0.8	0.6	6	0.9	1.52	0.76
2.2	0.9	9	2.0	2.41	1.21
4.8	1.3	13	2.2	2.28	1.14
9.1	1.8	18	4.8	2.74	1.37
18.7	2.4	24	9.1	3.68	1.84
31.4	2.9	29	19.0	4.43	2.22
			31.6	4.86	2.43

The data of Tables 1 and 2 are presented graphically in Figure 1, and it is clear from this figure that simple functions would satisfactorily express the variation of error with composition.

The solid lines in Figure 1 are representations of empirical equations derived from the data of Tables 1 and 2. These equations are of the type $y_z = ax^b$. Specifically:

$$y_{100} = 6.50x^{0.44}, \quad (1)$$

$$y_{1,000} = 1.32x^{0.28}, \quad (2)$$

$$y_{2,000} = 0.912x^{0.30}, \quad (3)$$

where x = per cent of desired constituent or 100 minus per cent of desired constituent, whichever is smaller, and y_z = error in parts per thousand for a count-length of z grains.

The dotted lines of Figure 1 show the variation of error with composition for the same three count-lengths, as indicated by normal distribution.* The distribution of error is so nearly normal at count-length of 100 grains that no empirical equation for the relation of composition and error would be necessary, confirming earlier work by Wildman. But the divergence of experimental error from normal distribution increases rapidly with count-length, and unadjusted normal distribution is not a reliable index of error even for count-lengths as short as 500. Generally, the normal probable error formula is used as a justification for rather short counts, the claim being that the decrease of error does not warrant undue extension of the count. "Undue" extension usually refers to anything over 400 grains. Not only is the counting error of a 400-grain count considerably less than expected from normal distribution, but the precision of a 1,000-grain count is so much better than that of a 400-grain count that the time consumed in extending the count is often well-spent. It should be remembered, however, that count-length cannot affect any but counting errors.

The development of a single equation expressing counting error as a function of composition level and count-length requires the correlation of the con-

* Probable Error $= 0.6745\sqrt{npq}$, where n = total frequency, p = probability of success, q = probability of failure; see Dryden (14), Krumbein and Pettijohn (21), or any statistics text.

stants a and b of equations (1), (2) and (3) with a third variable, the count-length, referred to throughout as z. From the first three columns of Table 3 it is clear that the variation of z with the empirical constants is reciprocal, and the very rapid variation of z as compared with a and b suggests the use of reciprocals of the roots of z. The correlation is accomplished here by the use of multiples of the reciprocals of the square root and four-tenths root of z, the u and v values of Table 3. In the discussion which follows, it is shown that for a very considerable range of count-length, a may be expressed as a power function of u, and the product ab as an exponental function of v; the second constant (b) being readily obtained from this latter function of the product of the two constants. These relations are neither unique nor all-inclusive. But equations based on them yield satisfactory correlation with experimental data for the critical range of count-length, and are simple to apply; for present purposes a more fundamental treatment is unnecessary.

TABLE 3.

z	a	b	$u = \frac{100}{z^{0.5}}$	$v = \frac{100}{z^{0.4}}$	$w = 10ab$
100	6.50	0.444	10.00	15.85	28.85
1,000	1.32	0.276	3.16	6.31	3.64
2,000	0.91	0.299	2.24	4.78	2.72

A relationship is easily established for a, in terms of u, as defined in Table 3 above. The equation of the line shown in Figure 2 is

$$a = 0.301u^{1.33}. \tag{4}$$

For the values of u shown above, calculated values of a deviate by no more than 6 per cent from the empirically derived estimates. It is possible that the relationship is not rigorously parabolic, but the indicated curvature is so slight that it could not be legitimately established from the data, and in any case it would have virtually no effect on calculated a values for z of less than 2,000.

The correlation of b with z can be accomplished by the use of the product ab, or, as shown in Table 3 and Figure 3, $w = 10ab$. The reversal of the sense in which b varies with z may be apparent rather than real, and those familiar with this type of work will immediately discover, in Figure 1, points whose omission from the calculations would have yielded a consistently inverse variation of b and z. Since this seemed the only justification for such omission, and it was not known that b ought to vary inversely with z throughout, all the data were retained.

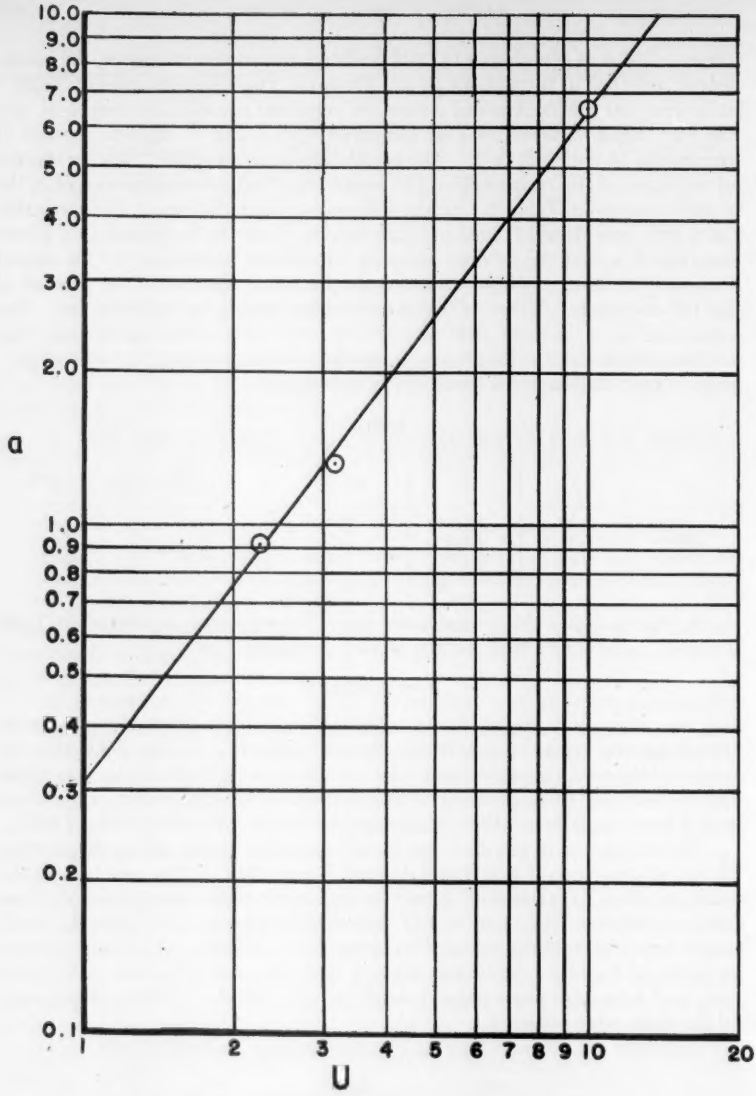
Using the definitions shown as column headings in Table 3, viz.:

$$u = \frac{100}{z^{0.5}}, \qquad v = \frac{100}{z^{0.4}}, \qquad w = 10ab,$$

$$\log w = -0.013 + 0.0927v \text{ (see Fig. 3)}, \tag{5}$$

or

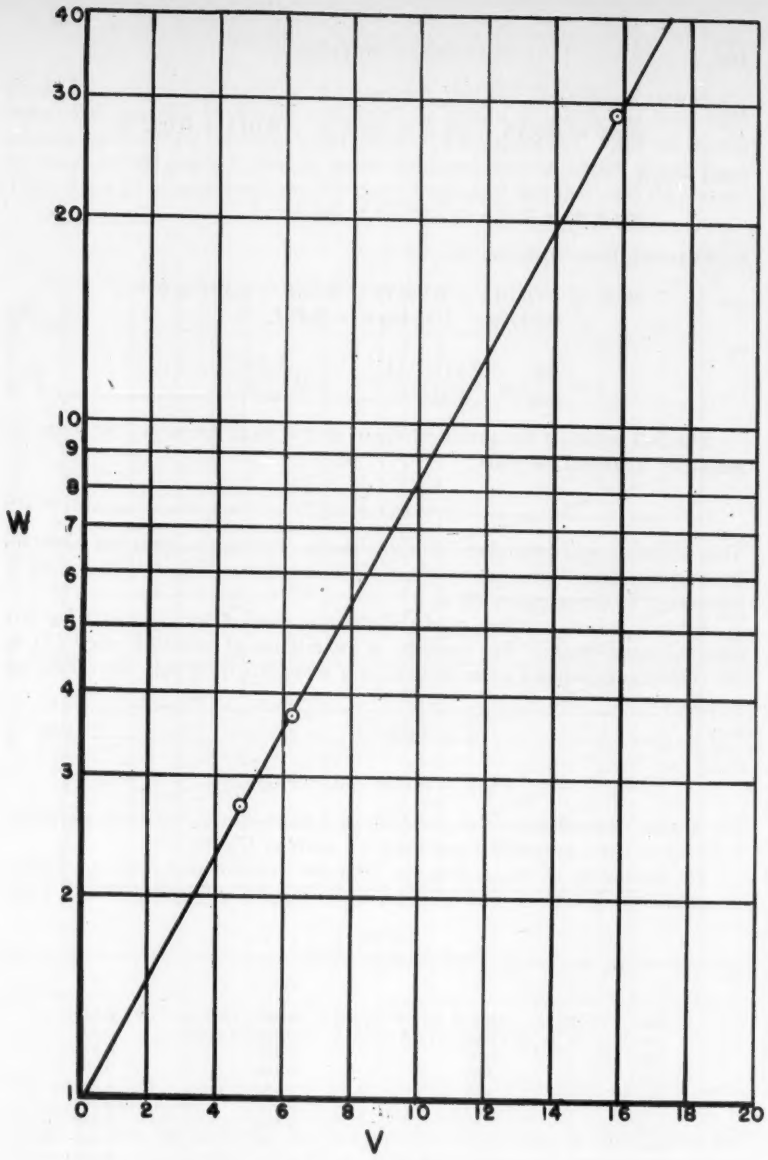
$$w = (0.97)(1.24)^v. \tag{5a}$$



$$U = \frac{100}{Z^{0.5}}$$

$$a = .301u^{1.33}$$

Figure 2— GRAPH OF EQ.(4) FOR CONSTANT "a" IN PRECISION EQUATION.



$$V = \frac{100}{Z^{0.4}}$$

$$W = 10\,ab$$

Figure 3— GRAPH OF EQ. (5a)

But,

$$\log w = \log 10 + \log a + \log b = -0.013 + 0.0927v,$$

from which

$$\log b = -0.013 + 0.0927v - \log a - 1.$$

Substituting from equation (4), for a

$$\begin{aligned} \log b &= -0.013 + 0.0927v + 0.522 - 1.33 \log u - 1 \\ &= 0.0927v - 1.33 \log u - 0.491, \end{aligned} \tag{5b}$$

or

$$b = \frac{w}{10a} = \frac{(0.97)(1.24)^v}{3.01u^{1.33}} = 0.32\,\frac{1.24^v}{u^{1.33}}. \tag{5c}$$

The full equation for precision error of the total, expressed in terms of parts per thousand, is, then:

$$y = ax^b = ax^{\frac{w}{10a}}. \tag{6}$$

This equation will reproduce the empirically developed equations with an error of less than 6 per cent in either of the constants. Most of this error is introduced in the equation for a.

Table 4, below, contains values of the constants of equation (6) for any practical count-length. For instance, if the relation of precision error (y) to per cent of constituent (x) is desired for a count-length of 900, the values are as follows:

$$y = 1.49x^{0.266},$$

or

$$\log y = 0.173 + 0.266 \log x.$$

For a more general picture of the over-all relationship of the three variables, it is best to use a graphical representation, such as Figure 4.

The derivation of values directly from the experimental data—to replace the computed values of Table 4—for count-lengths between 100 and 1,000

TABLE 4.

v	a	$\log a$	b
100	6.43	0.808	0.446
200	4.06	0.608	0.338
300	3.09	0.490	0.277
400	2.56	0.408	0.265
500	2.20	0.343	0.261
600	1.95	0.290	0.260
700	1.75	0.244	0.262
800	1.61	0.207	0.263
900	1.49	0.173	0.266
1,000	1.39	0.143	0.269
2,000	0.879	−0.056	0.307
4,000	0.552	−0.258	0.381
8,000	0.349	−0.457	0.500

would be useful. It is possible, for instance, that the precision of counts between 100 and 400 is slightly overstated in Figure 4, which has been constructed by inserting constants from Table 4 in equation (6). But for counts in excess of 500 grains in length, power functions with constants drawn from Table 4 are to be preferred, and for count-lengths of less than 500 they prob-

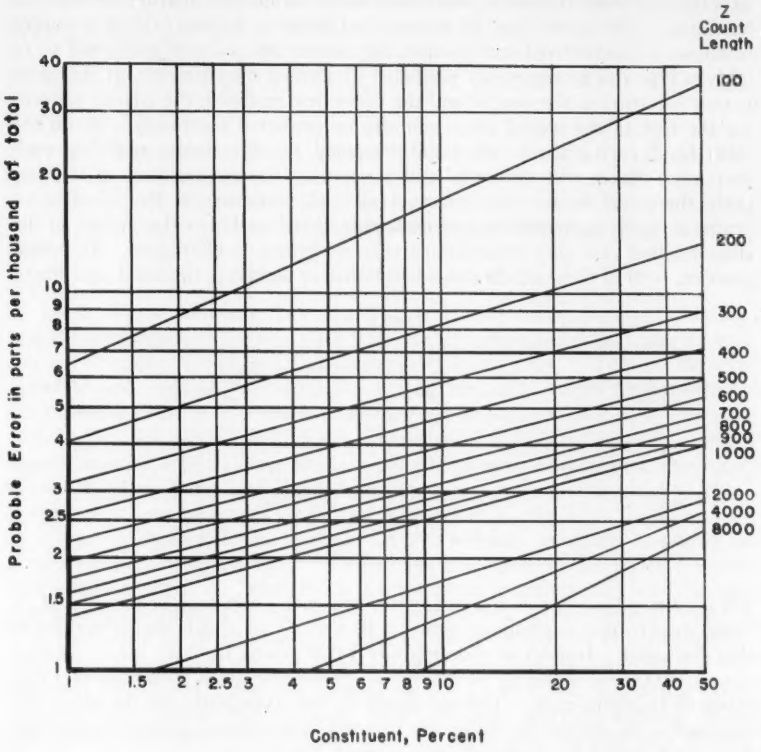


Figure 4—VARIATION OF ERROR WITH COUNT LENGTH, CONSTRUCTED FROM DATA IN TABLE 4.

ably give a better approximation of error than the theoretical probable error of normal distribution. Equation (6) yields impossible results for z values of 16,000 or over, but it checks the experimental data closely at 2,000 grains and extrapolation to z values of 4,000 or even 8,000 does not seem unwarranted. In any case, the validity of the general relation for counts of over 2,000 grains is academic at present, and will probably remain so for some time.

If we follow the usual convention of stating the error of a single analysis

in terms no smaller than the smallest unit of measurement—in this case 1 grain—the precision error due to counting will be about as shown below in Table 5.

In view of the widespread use of the normal probable error equation as an index of counting error, some rationalization of the discrepancy between the experimental data and error predictions based on normal distribution will not be amiss. The matter may be summarized about as follows: Given a sample of known (quantitative) composition, the chance that a single grain will be of a given type can be rigorously predicted by normal distribution. If the grain is now returned to the sample and the procedure repeated, the chance governing the type of the second grain can also be predicted rigorously. If, on the other hand, each grain is tallied and discarded, the uncertainty attending each successive choice will diminish, and concerning the composition of the last grain there will be no uncertainty at all. If, furthermore, the selection of grains is rigidly systematized and uniformly distributed over the surface of the slide, another and very considerable chance element is eliminated. In actual practice, both of these conditions are fulfilled as nearly as time and equipment

TABLE 5.

Precision Error % of total	Composition Range, x or $100-x$		
	$x = 500$	$x = 1{,}000$	$x = 2{,}000$
0.1		1.0– 1.4	1– 6
0.2	1.0– 1.7	1.4– 8.8	6–30
0.3		8.8–31.0	30–50
0.4	1.7–15.0	31.0–50.0	
0.5			
0.6	15.0–50.0		

will permit. No grain is counted twice, and each grain may be thought of as being chosen from a group of between 10 and 20, of which the remainder is also discarded. Instead of choosing any 1,000 grains from an initial population of 16,000, for instance, we attempt to choose one grain from each of 1,000 group of 16 grains each. This we surely do not accomplish, but the closer we approach it the greater the difference between experimental counting error and that which would be predicted from normal distribution.

It should be remembered that we are dealing here with counting error *per se*, all the data for a given composition level being taken from a single slide. Without experimental treatment or mathematical analysis of sampling, it is impossible to predict the size and type of the total laboratory error.

Potential Accuracy of the Counting Procedure.

Where internally consistent results are satisfactory—as in heavy mineral correlation, control analyses, etc.—knowledge of the precision of the count is all that is required. If, for any reason, it is desired to convert number frequencies into weight percentages—as in rock or ore analyses, analyses of final

mill-products, shape-factor studies, etc.—it will be necessary to convert equation (6), which is an expression for absolute (or what is here called precision) error, into a form in which it will exhibit relative error. In equation (6) y is already in terms of parts per thousand. If it is divided by the product $10x_r$, where x_r is the percentage of constituent reported by analysis, and the quotient multiplied by 100, the result will be a statement for relative error, *e.g.*:

$$y_r = \left(\frac{y}{10x_r}\right)\cdot 100 = \frac{10}{x_r}\,(ax^b) \tag{7}$$

or

$$\log y_r = 1 - \log x_r + \log a + b \log x, \tag{7a}$$

where

y_r = per cent relative error,
x_r = per cent of constituent reported by analysis,

and

x = x_r or $100 - x_r$, whichever is smaller.

By the use of equation (7a), for which necessary non-experimental values may be obtained from Table 4, the relative error due to counting may be extracted from any known total or partial laboratory error. With satisfactory sampling and counting techniques of known variance, it will be possible to evaluate the accuracy of frequency analysis by the usual method of comparison with known standards. Without a knowledge of sampling error an *a priori* consideration of relative error yields nothing but a minimum for total analytical error. Figures 5 and 6, which are included here only for the sake of comparison with previous work, should be considered in this light.

Figure 5 duplicates and extends Dryden's figure, generally available in Krumbein and Pettijohn (21). The curves are based on the probable error of normal distribution. Figure 6 is an analogous chart constructed from the relationships developed in this paper. Dryden's analysis is consistent only if it is considered as an estimation of counting-error proper, in which case Figures 5 and 6 are directly comparable, and it is clear that counting-error is not normally distributed. The use of count-length as an index of counting-error requires experimental evaluation for each particular counting method. It is conceivable that the error of some counting techniques may greatly exceed predictions based on normal distribution; for the method described here, the error is in general far less than that which would be expected from normal distribution.

Conclusion.

The critical range for number-frequency analysis by the method described in this paper is between 500 and 2,000 grains. The increased accuracy of a 1,000-grain count as opposed to one of 500 grains is often worth obtaining, but extension of the count-length beyond 1,000 is rarely worth while.

It should be remembered that the absolute number of grains counted is without significance, except for very short counts. The mount contains a

finite number of grains, and, other factors being equal, it is the ratio of grains counted to grains mounted which determines the error. Experimental counts which form the basis for this paper were made on 100–200 mesh sand. For equal weights of coarser material, the error is smaller, for equal weights of finer material, greater, than that shown in Figure 6.

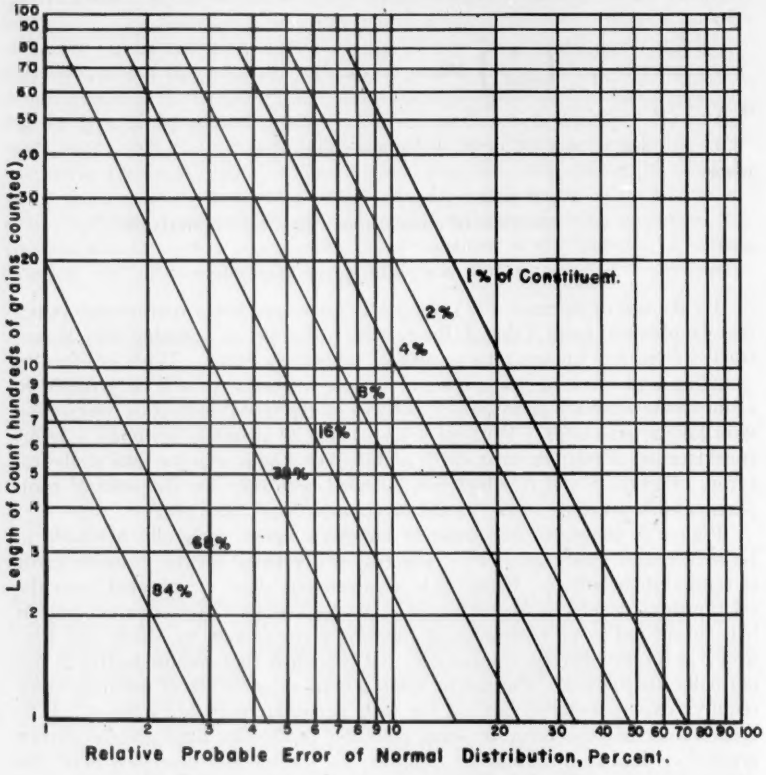


Figure 5— RELATIVE COUNTING ERROR, BASED ON NORMAL DISTRIBUTION.

In general, it may be said that *as far as the count itself is concerned,* the precision of petrographic analysis by grain-count is comparable to that of the operations of commercial chemical analysis. It must be emphasized that the relations established in this paper express only the error due solely to counting, and permit no generalization concerning either total analytical error or partial errors except those introduced by the count. Errors due to sizing, sampling, shape differences, etc. require separate experimental or analytical

treatment. A study of micro-sampling is now in progress, and a description of the procedure will be published as soon as data can be accumulated concerning its error.

The utility of a standardized fragment analysis procedure of known variance scarcely requires comment. By its use number frequencies can readily

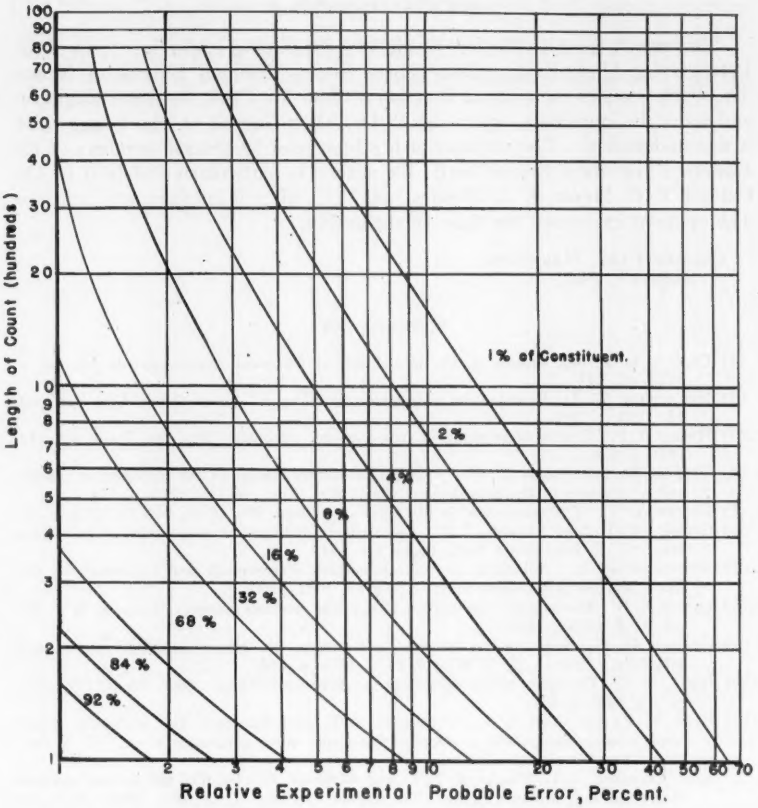


Figure 6— RELATIVE COUNTING ERROR, EXPERIMENTAL

be converted to weight percentages of equal reliability, the error inherent in other petrographic operations can be properly evaluated, and empirical shape factors can be developed where necessary.

As long as modal analyses are made from thin sections, sampling will be subject to large and unpredictable errors due to grain size, mineral fabric and,

most important, thin-section area. With a properly standardized technique of fragment analysis, petrographic sampling of all but the finest-grained materials can be put on a par with sampling for chemical analysis; its only limits will be the time and money available for its prosecution—and these are ultimately a function of the importance attached to the project.

ACKNOWLEDGMENTS.

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COLLEGE PARK, MARYLAND,
August 9, 1944.

REFERENCES

(1) Chamot, E. M., and Mason, C. W. Handbook of Chemical Microscopy, 2d ed., vol. 1, 1932, ch. XIV.
(2) McCaughey, W. J. Examination of commercial feldspar. Trans. Amer. Cer. Soc., vol. 15, 1913, p. 381.
(3) Hynes, D. P. Degree of crushing of free economic minerals. Min. Sci. Press, vol. 110, 1915, p. 944.
(4) Thomas, K., and Apgar, F. W. Approximate determination of the minerals in concentrates by means of the microscope. Chem. Met. Eng., vol. 18, 1918, p. 514.
(5) Clayton, C. Y. The microscope in ore dressing. Chem. Met. Eng., vol. 19, 1918, p. 61.
(6) Coghill, W. H., and Bonardi, J. P. Approximate quantitative microscopy of pulverized ores. U. S. Bur. Mines Tech. Paper 211, 1919.
(7) Schneiderhöhn, H. Anleitung zur mikroskopischen Bestimmung und Untersuchung von Erzen und Aufbereitungsprodukten. Berlin, 1922, p. 32.
(8) Larsen, E. S. Microscopic examination of raw and calcined gypsum. Proc. A. S. T. M., vol. 23, I, 1923, p. 236.
(9) Gardner, H. F. Notes on the chemical and microscopic determination of gypsum and anhydrite. Proc. A. S. T. M., vol. 26, I, 1926, p. 296.
(10) Insley, H. I. The quantitative microscopic analysis of feldspar. Jour. Amer. Cer. Soc., vol. 10, 1927, p. 651.
(11) Head, R. E., Crawford, A. L., Thackwell, F. E., and Burgener, G. Statistical microscopic examination of mill products of the copper queen concentrator, etc. U. S. Bur. Mines Tech. Paper 533, 1932.
——, Crawford, A. L., Thackwell, F. E., and Burgener, G. Detailed microscopic analysis of ore and mill products of the Utah Copper Co., etc. U. S. Bur. Mines Rept. Investigations 3288, 1935.
——, Crawford, A. L., Thackwell, F. E., and Christensen, A. L. Statistical microscopic study of ores and mill products from the Anyox Plant, Brit. Col., etc. U. S. Bur. Mines Rept. Investigations 3290, 1935.
(12) Thomson, E. Quantitative microscopic analysis. Jour. Geol., vol. 38, 1930, p. 193.
(13) Wildman, J. D. A statistical study of some sampling relations with special reference to quantitative microscopy. Jour. Ass'n Off. Agr. Chem., vol. 14, 1931, p. 563.
(14) Dryden, A. L. Accuracy in percentage representation of heavy mineral frequencies. Proc. Nat. Acad. Sci., vol. 17, 1931, p. 233.
(15) Thackwell, F. E. Quantitative microscopic methods with an integrating stage, etc. ECON. GEOL., vol. 28, 1933, p. 178.

(16) Glagolev, A. A. On the geometrical methods of quantitative mineralogic analysis of rocks. Trans. Inst. Econ. Min., Moscow, vol. 59, 1933.
——. Quantitative analysis with the microscope . . . by the "point" method. Eng. Min. Jour., vol. 135, 1934, p. 399.
(17) Rept. of the Comm. on Access. Minerals, 1936–37, National Research Council (A. N. Winchell, F. F. Grout, G. Tyler, R. W. Marsden).
(18) Faust, G., and Gabriel, A. Petrographic methods and their application to the examination of non-metallic minerals. U. S. Bur. Mines Inf. Circ. 7129, 1940.
(19) Willman, H. B. Feldspar in Illinois sands. Ill. State Geol. Surv., Rept. Investigations 79, 1942, p. 10.
(20) Faust, G. T. The differentiation of magnesite from dolomite in concentrates and tailings. Econ. Geol., vol. 39, No. 2, 1944, p. 142.
(21) Krumbein, W. C., and Pettijohn, F. J. Manual of Sedimentary Petrography. Appleton-Century, New York, 1938, p. 472.

OXIDATION OF PRIMARY NICKEL SULPHIDES.[1]

C. E. MICHENER AND A. B. YATES.

ABSTRACT.

The weathering of diamond drill core shows how violarite is rapidly formed from pentlandite and subsequently leached by further oxidation. The formation of nickeliferous pyrite and marcasite as alteration products after pyrrhotite is discussed and various reactions suggested. An experiment designed to artificially weather the nickel-bearing sulphides shows that the formation of sulphuric acid in the system destroys the product of oxidation unless it is continuously removed as in normal weathering.

In a study of the orebodies of the Sudbury District, numerous occurrences of partially oxidized ore have been observed in which the process has not gone to completion and the intermediate products of oxidation could be studied. That the oxidation of primary nickel-bearing sulphides is a relatively rapid one is borne out by the fact that sulphides found in abandoned mine dumps and diamond drill core are in an advanced state of oxidation after being exposed for a period of twenty-five years or less. The amount of oxidation in a glaciated region such as Sudbury is of course small and the secondary sulphides formed are mainly of scientific interest.

The primary sulphides with which we are concerned are pentlandite $(FeNi)_9S_8$, magnetic pyrrhotite $FeS_{1.14+}$, non-magnetic pyrrhotite $FeS_{1.14-}$, pyrite, chalcopyrite and cubanite. Other primary nickel ores such as parkerite [2] and the arsenides of nickel are too rare to be considered here The sulphides polydemite and Heazlewoodite have not been found in this district.

Pentlandite in the Sudbury area has a constant composition irrespective of the type of ore from which it is obtained. An analysis of Sudbury pentlandite and one from Kamikivitunturi, Finland are given below, calculated to 100 per cent.

	Ni	Fe	S
Creighton Mine, Sudbury	35.75	31.45	32.80
Kamikivitunturi, Finland	35.23	31.80	32.97

The formula worked out from these and other assays in the district is $(FeNi)_9S_8$. It is also interesting to note the work of M. Lindqvist, D. Lundqvist and A. Westgren,[3] also I. N. Chirkov [4] who find similar atomic ratios for the mineral.

[1] Published by permission of the International Nickel Co. of Canada Ltd.

[2] Michener, C. E., and Peacock, M. A.: Parkerite ($Ni_3Bi_2S_2$) from Sudbury, Ontario, redefinition of the species. Amer. Min. 28: 343–355, 1943.

[3] Lindqvist, M., Lundqvist, D., and Westgren, A.: The crystal structure of Co_9S_8 and of pentlandite $(Ni, Fe)_9S_8$. Stockholms Högskola, Inst. Gen. and Inorg. Chemistry, June 1936.

[4] Chirkov, I. N.: Pentlandite from the copper-nickel deposit of Mouche-Tundra. Comptes Rend. de L'Acad. des Sci. de L'U. R. S. S., Vol. 29, 1940.

There are two varieties of pyrrhotite, differing in magnetic properties. The non-magnetic variety always has a sulphur content below $FeS_{1.14}$ and becomes ferro-magnetic when the sulphur is above this figure. Both varieties occur in the same orebodies but the non-magnetic type is generally confined to the offset deposits.[5]

Primary pyrite is relatively unimportant in amount. Chalcopyrite and cubanite do not enter into the discussion as they generally remain unaltered until after the cycle of nickel oxidation is complete.

Violarite. The origin of violarite has been in question until recently Sandefur [6] and later Dennen [7] have shown it to be a replacement of pentlandite. Earlier Lindgren and Davey [8] considered "violarite" to be the result of the circulation of surface waters. Later Short and Shannon [9] showed that the "polydemite" of the Sudbury District was really violarite but considered it to be hypogene.

About thirty-five years ago diamond drilling was done at the Victor property on the East Range of the Sudbury Basin. Sulphide ore was encountered, but the core was evidently not sampled, and left in the boxes on the ground. The latter rapidly rotted away leaving the core exposed to weathering for a period of perhaps twenty-five years. The junior author discovered this core early last year and studies were subsequently made on the alteration products. In view of the fact that recent drilling has shown the presence of fresh unaltered sulphides at the same site this proved especially interesting.

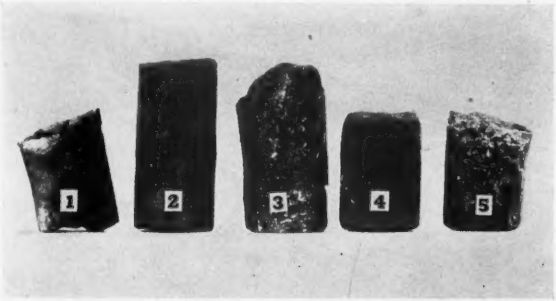


FIG. 1. Core showing various stages of oxidation of the sulphide.

Specimens of the core in various stages of alteration are shown in Figure 1, the more oxidized pieces showing a greater degree of swelling. The first sign of alteration in the core is the development of violarite along cleavage cracks

[5] Offset deposits—Sulphides associated with quartz diorite dikes as opposed to those on the rim of the nickel eruptive.

[6] Sandefur, B. T.: The geology and paragenesis of the nickel ores of the Cuniptau Mine, Goward, Nipissing District, Ontario. ECON. GEOL. 37: 173–187, 1942.

[7] Dennen, W. H.: A nickel deposit near Dracut, Mass. ECON. GEOL. 38: 25–55, 1943.

[8] Lindgren, Waldemar, and Davy, W. M.: Nickel ore from Key West Mine, Nevada. ECON. GEOL. 19: 309–319, 1924.

[9] Short, M. N., and Shannon, E. V. Violarite and other rare nickel sulphides. Amer. Min. 15: 1–22, 1930.

in the pentlandite. Two stages in this process are shown in Figures 2 and 3. Toward the completion of this stage the pyrrhotite begins to develop cracks in which limonite is deposited. These gradually widen as shown in Figures 5

FIG. 2. Large crystal of pentlandite (white) partly replaced by violarite (dark gray). × 157.

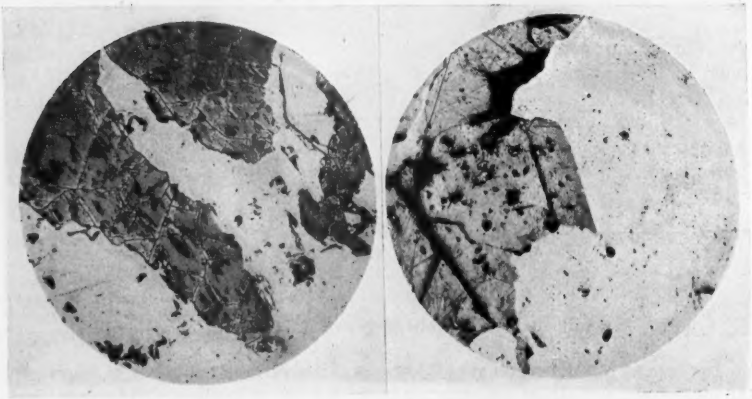


FIG. 3. (Left) Pentlandite (gray) in field of unaltered pyrrhotite (light gray). The pentlandite shows initial stage of violarite replacement. × 172.

FIG. 4. (Right) Fresh pentlandite (gray) in pyrrhotite (white) from recent drilling. × 172.

and 6. At this point the pentlandite is all replaced by violarite which then starts to leach out. By the time the pyrrhotite is half oxidized, the violarite (and pentlandite) is practically all removed by solution. Up to this point the

chalcopyrite has remained unaltered and is the last of the three sulphides to be attacked. The final product is limonite practically free of nickel and with very little copper. From a study of polished sections it was found that the violarite always formed within the limits of the pentlandite grains.

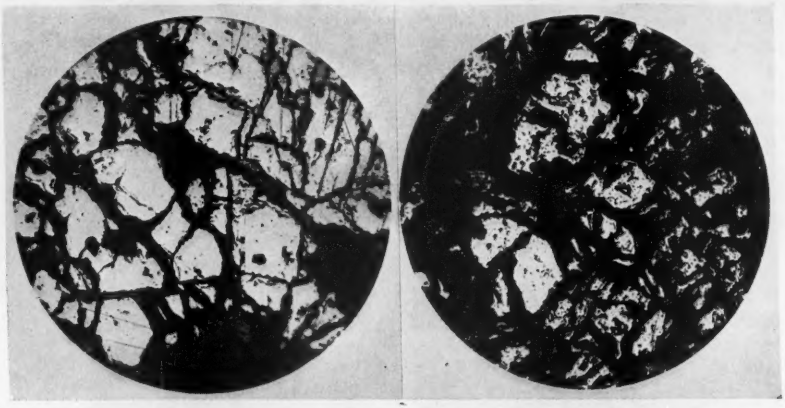


FIG. 5. (Left) Pyrrhotite (white). Cracking and veining by limonite just starting. × 58.

FIG. 6. (Right) Pyrrhotite (white) largely altered to limonite (black areas). Chalcopyrite still fresh and violarite largely removed at this stage. × 58.

The oxidation of pyrrhotite and the solution of violarite which appears to accompany this process permits the conclusion that violarite is an intermediate product which is only stable in a certain limited range of oxidation. In working with samples of weathered outcrops of nickel ore, it has been found that the color of violarite is variable. Identical X-ray powder patterns have been obtained from the typical violet colored mineral and also from polished samples grading toward the brassy color of pentlandite. This may be due to variations in the iron-nickel ratio. X-ray powder patterns of violarite from the Vermilion Mine (material from here was analyzed by Short and Shannon) and violarite from oxidized core described above are identical and of the spinel type.

Millerite. We have noted millerite from one locality only in the Sudbury District. This ore was described by Short and Shannon and our observations are in agreement with theirs, namely, that the millerite replaces the violarite. Special conditions of oxidation must have prevailed there as the violarite, instead of going over directly to limonite, went through the intermediate stage of iron removal to form millerite.

Secondary Ores at Greater Depth. At one of the operating mines in the district post-ore faulting occurs. Where the fault intersects sulphides an interesting group of secondary minerals have formed. The fault is open and considerable water drains down through it to the lower levels. On each side of the fault for a distance of about 35 feet the primary sulphides, pentlandite,

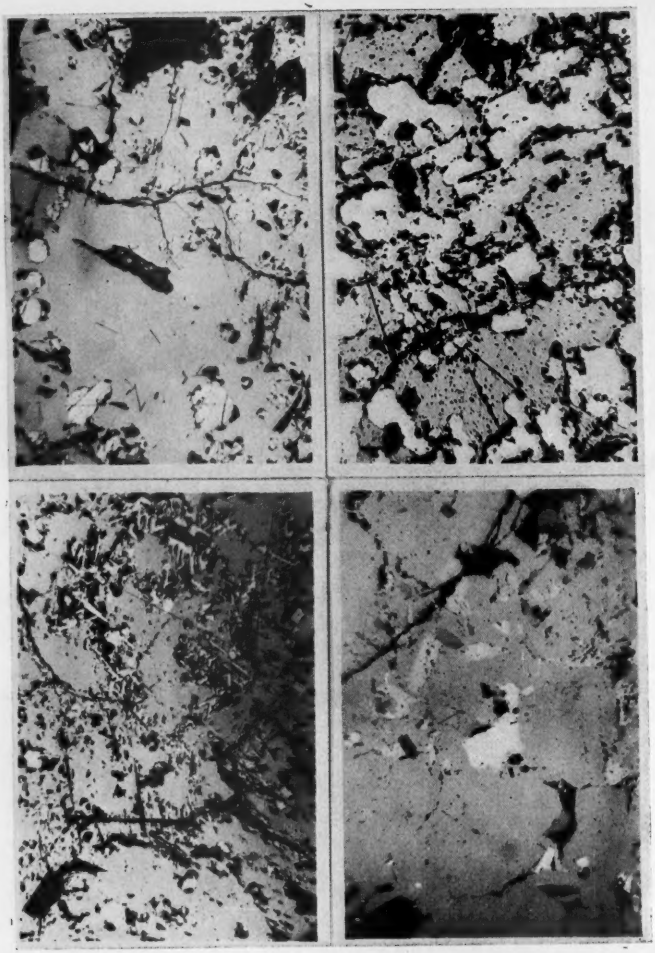


FIG. 7. (Upper left) Pyrrhotite (gray background) replaced by pyrite (small white areas). Note connecting fractures. × 87.

FIG. 8. (Upper right) More advanced stage of Figure 7. Pyrrhotite gray, pyrite white. × 87.

FIG. 9. (Lower left) Pyrrhotite (gray background) replaced by marcasite (white blades). A few replacing pyrite grains are also present. × 87.

FIG. 10. (Lower right) Complete replacement of pyrrhotite by pyrite and marcasite. Gray background is pyrite. Light and dark blades are marcasite. This is the completed stage of Figures 7, 8 and 9. Nicols crossed. × 87.

pyrrhotite and chalcopyrite have undergone varying degrees of alteration down to a known depth of 1,400 feet.

Pyrite forms by direct replacement of the pyrrhotite. Three stages in this process, taken in the transition zone from primary to secondary ores, are shown in Figures 7, 8 and 10. The pyrite first appears as isolated plums in the pyrrhotite, being connected by cracks and solution channelways (Fig. 7). These grow at the expense of the pyrrhotite but with an apparent volume shrinkage (Fig. 8).

Marcasite, which is present in almost equal volume throughout the altered zone, starts along cracks and advances as blades along parting planes or crystallographic boundaries. This type of replacement is shown in Figure 9. In the same photomicrograph centers of pyrite growth may be seen, and it appears that the two types of replacement went on simultaneously until all the pyrrhotite had been replaced. The final stage in this process is shown in Figure 10. The field consists entirely of pyrite enclosing blades of marcasite.

In the replacement of pyrrhotite by pyrite and marcasite a small amount of nickel was taken up by the replacing minerals and is believed present in atomic substitution. The X-ray patterns, however, do not show a shift in spacing sufficient to be noticeable. Repeated microchemical tests on polished sections of both pyrite and marcasite gave a nickel reaction. Small samples scratched from the polished surface of these two minerals ran about 2 per cent nickel.

Violarite was found in the pyrite-marcasite ores but its origin is more obscure than that of the diamond drill core. There is evidence that this violarite (and small amounts of millerite) was formed by solutions which carried the nickel in the form of soluble salts some distance before deposition. Some of the violarite is deposited as fairly compact crystalline aggregates, but grades into mixtures which consist of a black, earthy, gouge-like matrix impregnated with minute grains of violarite.

Chalcopyrite, sphalerite and galena were observed in these ores but are unaltered primary sulphides. This agrees with the results found in the diamond drill core where chalcopyrite was found to be much more stable than the iron and nickel-iron sulphides.

Bravoite. The natural minerals occurring in the series FeS_2–NiS_2 have been described by Bannister [10] and later Peacock and Smith.[11] These authors have shown that there is a series between pyrite and bravoite with 25 per cent nickel in which the size of the unit cell increases with increasing nickel content. Undoubtedly our nickeliferous pyrite belongs in this series but with such a low amount of nickel that the difference in spacing cannot be observed. The former author suggested that a series of synthetic fusion products from FeS_2 to NiS_2 might corroborate this evidence. It so happened that such a series had been prepared at this laboratory for another purpose. The charges were fused in evacuated silica glass tubes, sealed with an oxygen-acetylene torch.

[10] Bannister, F. A.: Bravoite from Mill Close mine, Derbyshire. Min. Mag. 25: 609–614, 1940.

[11] Peacock, M.A., and Smith, F. G.: Precise measurements of the cube edge of common pyrite and nickeliferous pyrite. Univ. of Toronto Studies, No. 46, Contributions to Canadian Mineralogy, 1941.

Polished sections and X-ray patterns of the products showed that although FeS_2 and NiS_2 were homogeneous products all intermediate members consisted of a mechanical mixture of the two without any observable solid solution.

In the Sudbury ores primary pyrite is nickel free, but the secondary pyrite is often nickel bearing. Thomson,[12] Rasor[13] and Bannister[14] all describe concentric and radiating structures in their nickeliferous pyrite and bravoite. It thus appears likely that these two minerals are most likely to be found only as supergene products. The fusion products do not prove this but support the latter conclusion. It is interesting to note what I. N. Chirkov[15] says in speaking of the secondary minerals of the Monche-Tundra deposit: "In the zone of cementation a number of secondary minerals are developed of which the greatest interest is presented by bravoite—a secondary mineral after pentlandite."

Laboratory Experiments. An experiment designed to give a qualitative idea of the reactions taking place in the oxidation of iron and nickel sulphides was set up as follows. A filter tube packed with glass wool in the bottom was placed in an upright position and a quantity of broken pentlandite, pyrrhotite and chalcopyrite placed therein. Below this, a beaker was placed which contained the oxidizing solution. From the solution to the top of the funnel a tube was fitted in which a slow stream of air was forced by means of a fine jet fitted into the tube below the level of the solution. A continuous stream of solution and air thus circulated over the sulphides and returned to the beaker. The solution was made up of 65 parts per million divided equally between ferrous and ferric iron in the form of the sulphate, and brought to a pH of 2 with sulphuric acid.

The first noticeable change after several weeks was a bluish black coating on the pentlandite. The solution was then warmed by placing the beaker in a warm water-bath, approximately 60° C. Evaporation was taken care of by addition of distilled water when required. After several more weeks the sulphides and solutions were examined. The solution had increased in acidity from a pH of 2 to a pH of 0.8. The iron content increased from 65 to 1,207 parts per million, mostly ferric sulphate. (Ferrous sulphate is readily oxidized to the ferric state.) The solution had also taken up 636 parts per million of nickel in the form of nickelous sulphate. As the chalcopyrite appeared unchanged no determination for copper in the solution was made. The pentlandite had a bluish black film which appeared to corrode the grains. At several protected points (against silicate grains for example) minute remnants of the bluish coating remained and appeared much like violarite in polished section although the quantities were too small to obtain X-ray patterns. The pyrrhotite had in most cases acquired a rough surface covered with pyrite. In some instances the pyrite had entered cracks in the pyrrhotite. The new products thus formed are sulphuric acid, ferric and ferrous sulphate, nickelous sulphate, pyrite and probably violarite.

[12] Thomson, Ellis: Some ore minerals of the Denison Mine. Univ. of Toronto Studies No. 41. Contributions to Canadian Mineralogy, 1938.

[13] Rasor, C. A.: Bravoite from a new locality. Econ. Geol. 38: 399–407, 1943.

[14] Bannister, F. A.: op. cit.

[15] Chirkov, I. N.: Mineralogy of Monche-Tundra Compt. Rend. de L'Acad. des Sci. de L'U. R. S. S., Vol. 25, 1939.

These experimental data corroborate the findings of Gilbert [16] who quotes Allen [17] concerning the following reactions.

$$FeS \cdot S_x + H_2SO_4 = FeSO_4 + H_2S + S_x = H_2SO_4 + FeS_2$$

The presence of nickelous sulphate in the solution might result in the following:

$$(xNiSO_4 + yFeSO_4) + H_2S + S = H_2SO_4 + (xNiyFe)S_2 \text{ (bravoite)}$$
$$3(NiSO_4 + FeSO_4) + 3H_2S + S = 3H_2SO_4 + (NiFe)_3S_4 \text{ (violarite)}$$
$$NiSO_4 + H_2S = H_2SO_4 + NiS \text{ (millerite)}$$

It seemed a simple matter to check these reactions in the laboratory. Aqueous solutions of ferrous and nickelous sulphate were made up, each with a concentration of 5 gms. metal per liter. The pH of the former was 3.7 and of the latter 4.1. These were mixed in the following proportions.

1. nickelous sulphate solution
2. equal parts of nickelous and ferrous sulphate
3. 10 parts ferrous sulphate to 1 part nickelous sulphate

The three solutions were treated with hydrogen sulphide and the sulphide precipate examined. No. 1 proved to be NiS, the structure being identical with synthetic NiS formed by fusing nickel and sulphur in a closed tube. The structure is quite different from millerite. Nos. 2 and 3 were amorphous mixtures of iron and nickel sulphide and gave no X-ray powder pattern.

The filtered solutions which still contained considerable nickel and iron were again treated with hydrogen sulphide but no precipitate formed. The pH of the filtrates was 1.7, 2.7 and 2.9 respectively.

In the experiments just described there is no provision for the removal of sulphuric acid as would be the case under normal weathering conditions. In such a closed system it appears likely that the rapid build-up of sulphuric acid would destroy the violarite almost as quickly as it formed, leaving only a thin reaction film between the pentlandite and the solution. In other words, the reaction is reversible and could only continue by the removal of more sulphide unless there was continuous removal of the sulphuric acid, and a correct pH balance maintained in the oxidizing solutions. This probably accounts for the rapid oxidation of the violarite in the case of the weathered diamond drill core.

Discussion. Pyrite, some of it nickel-bearing, has been found replacing pyrrhotite at many gossan outcrops in the district as well as along the open fault described above. Violarite is less common for if the oxidation is too severe it is removed. Violarite has never been found in primary ores where there is no sign of oxidation. Both pyrite and violarite have a higher sulphur content than the mineral from which they formed. It was long known that sulphuric acid was one of the products of oxidation and the anomalous condition where sulphur was being built up and removed at the same time was of

[16] Gilbert, G.: Oxidation and enrichment at Ducktown, Tenn. A. I. M. E. Trans. 70: 998–1023, 1924.

[17] Allen, E. T.: Studies on ore deposition with special reference to the sulphides of iron. Jour. Wash. Acad. Sci. 1: 6, 1911.

much interest. Millerite and bravoite (if our nickeliferous pyrite can be called bravoite) would fall in the same category.

Hydrogen sulphide and pyrrhotite will form pyrite but with a volume increase. Our polished sections show on the other hand that there has been a volume shrinkage during its formation. This is readily explained by the removal of part of the iron and sulphur in the form of sulphuric acid and iron sulphates. The same reasoning would apply to the other iron and nickel sulphides.

The writers wish to thank officials of the International Nickel Co. of Canada Ltd. for permission to publish this paper. Our thanks are also due other members of the Geological Department who assisted in many ways in the location and collection of specimens.

COPPER CLIFF, ONTARIO,
April 24, 1944.

SEVENTH EDITION OF DANA'S "SYSTEM OF MINERALOGY."[1]

PAUL F. KERR.

FEW books have exerted so wide an influence over the science in which they have been written as Dana's System of Mineralogy. Notwithstanding the fifty-two years which have elapsed since the sixth edition was published and the twenty-nine years since the last appendix appeared, this great book has continued to be one of the most useful and convenient sources of data in the science of mineralogy. Thus the appearance of the seventh edition is a special event which arouses even more interest, because it has been known for some time that Professor Palache and his able co-workers have been concentrating their attention on the revision.

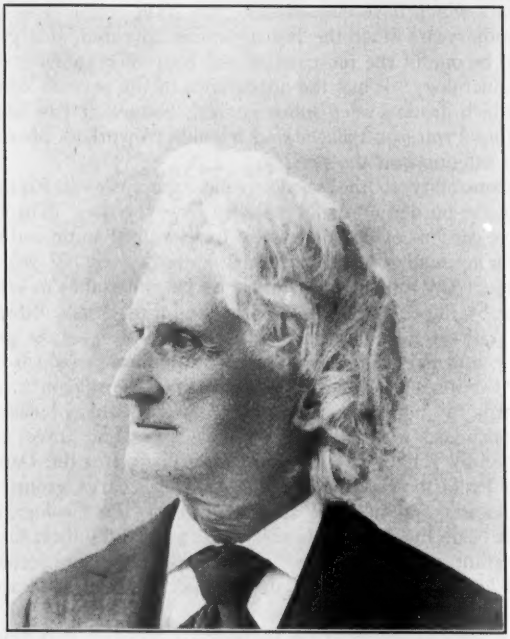
The responsibility to the science which the Seventh Edition carries is broader than the burden normally assumed by a revision. Through the years the successive editions of Dana's System have steadily improved until the year 1944 finds an accumulated heritage which extends over 107 years of mineralogical history. Any mineralogical worker who undertakes to bear the burden so ably borne by James Dwight Dana, George Jarvis Brush, Edward Salisbury Dana, and William E. Ford assumes no light load. To the publishers this edition is a centennial anniversary for Dana publication which dates back to the Second Edition of 1844. It represents a just pride in a service which greatly exceeds the normal contribution of the publishing business. All volumes and appendices with the exception of editions one, three, and four have been published by John Wiley & Sons. The project of the Dana revision as proposed by Professor Palache was endorsed by a large group of contemporary mineralogists and adopted as a project by the Geological Society of America. It bears the distinction of having received the most liberal award of any project grant yet made under the Penrose Fund of the society. Without this support and the assistance of the Holden Fund of Harvard University the revision would not have been possible.

While the responsibilities of the revision are weighty, it is most pleasing to observe that the authors have been thoroughly equal to the task. The standard of excellence of the previous editions has not only been retained but the authors have gone far beyond to add the imprint of their own efforts. The pattern already so well developed has lost none of its strength, while woven into that pattern are the most recent developments of modern scientific mineralogy to which the writers themselves have contributed so much. A simple revision confined entirely to the literature which might have satisfied many has not been accepted. In many cases supplementary scientific contributions have been carried through, even leading to independent publication in order to establish

[1] *Dana's System of Mineralogy*. Seventh Edition, Vol. 1. By Charles Palache, Harry Berman and Clifford Frondel. Pp. 834; Figs. 354. John Wiley & Sons, Inc., New York, N. Y.

the background of information considered necessary for the System. This lends a quality to the revision which raises it well above the level ordinarily attained even by good reference books.

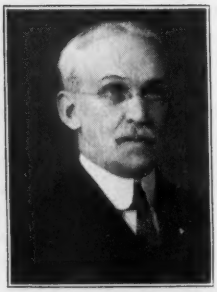
The seventh edition had just entered distribution when Professor Harry Berman was killed in a plane crash at Prestwick, Scotland. He had left the United States less than twenty-four hours earlier on a war time mission. The loss of an author of such brilliance who had every reason to look forward to many years of mineralogical achievement is one of the unfortunate sacrifices of the war.



JAMES DWIGHT DANA

1813–1895

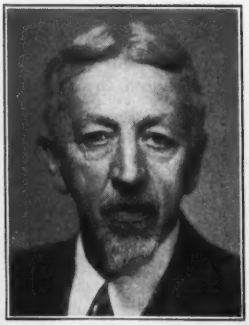
The First Edition of Dana's System of Mineralogy (1837), comprising 452 pages and including an appendix of 119 pages, was published by Durrie and Peck and Herrick and Noyes in New Haven. The treatise was written by James Dwight Dana, then an assistant in the Department of Chemistry, Mineralogy and Geology in Yale College. Dana felt that the progress of Mineralogy in this country and in England had been tardy in contrast to the rapid advancement on the continent of Europe. The System was published, as he expressed it, in "the hope of filling up, in some degree, the existing blank in



E. S. Dana
1849–1935

George J. Brush
1831–1912

William E. Ford
1878–1939



Charles Palache
1869–

Harry Berman
1902–1944

Clifford Frondel
1907–

certain departments of American Mineralogical Science by combining the various excellencies of the most valuable works on the science." The progress of mineralogy was such that seven years after the System was first published a second edition was assembled and published by Wiley and Putnam, New York and London (1844). This marked the first contact of the present publishers with Dana's System. The second edition contained 633 pages and represented a considerable advance over the earlier volume.

A third edition (1850) which enlarged the book to 711 pages was published by George P. Putnam, New York and London. In this edition the system began to develop the organization of material suggestive of later editions. The fourth edition (1854) was published by D. Appleton & Co., New York, under the date of 1858. By that time Dana had become Silliman Professor of Natural History in Yale College. This edition was divided into Part 1, Crystallography, or the science of the structure of minerals, and Part 2, a System of Mineralogy, comprising the most recent discoveries. The two together comprised 953 pages.

In the fifth edition (1868) Dana was aided by Professor George Jarvis Brush, Professor of Mineralogy and Metallurgy in the Sheffield Scientific School of Yale College. Both names appeared on the title page. The publisher John Wiley & Son, at that time at 2 Clinton Place, New York, has continued to publish Dana's System since that time. Appendices to the fifth edition appeared at intervals following the original publication. The first appendix was written by Professor Brush (1872). The second appendix (1875) was written by Edward Salisbury Dana, son of James Dwight Dana, and then curator of Mineralogy of the Peabody Museum, Yale College. He also wrote a third appendix (1882). The fifth edition and three appendices together comprised 1044 pages. It represented the emergence of the System of Mineralogy into the pattern now so familiar to all mineralogists as developed by Edward Salisbury Dana in the sixth edition (1892). By that time in addition to being Curator of Mineralogy the younger Dana had become Professor of Physics in Yale University. The sixth edition, together with its three appendices, has been the Dana's System of the last half century in American Mineralogy. The first appendix (1899) was written by Dana, the second (1909) by Dana and William E. Ford, Professor of Mineralogy, Sheffield Scientific School of Yale University. The third appendix (1915) was written entirely by Professor Ford. The sequence of authorship and the various editions with which they have been associated are summarized below:

THE SUCCESSION OF DANA AUTHORS

James Dwight Dana—First Edition 1837; Second Edition 1844; Third Edition 1850; Fourth Edition 1854.
James Dwight Dana and George Jarvis Brush—Fifth Edition 1868.
George Jarvis Brush—First Appendix (Fifth Edition) 1872.
Edward Salisbury Dana—Second and Third Appendices 1875 and 1882. Sixth Edition 1892; First Appendix 1899.
Edward Salisbury Dana and William E. Ford—Second Appendix 1909.
William E. Ford—Third Appendix 1915.
Charles Palache, Harry Berman and Clifford Frondel—Seventh Edition, Volume 1, 1944.

The volume which has just appeared and is known as Volume I of the Seventh Edition is the first of three volumes two of which are yet to be published. The division of the subject matter between the three volumes is, I—elements, sulfides, sulfosalts, oxides, II—halides, carbonates, sulfates, borates, phosphates, arsenates, etc., III—silica, silicates. Volume II is reported to be in preparation and it is understood that progress has already been made in the assembly of material for Volume III. Unfortunately, according to the authors the second two volumes will be delayed by the war.

The form of classification adopted for the Seventh Edition makes effective use of modern studies in crystal chemistry. The minerals are divided into eight classes: (1) elements, (2) sulfides, (3) sulfosalts, (4) simple oxides, (5) oxides containing uranium, thorium and zirconium, (6) hydroxides, (7) multiple oxides, (8) multiple oxides containing columbium, tantalum and titanium. Each class is divided according to either AmXn or AmBnXp types, where A stands for positive ions (cations) or electropositive atoms, and X for negative ions (anions) or electronegative atoms. In multiple oxides the arrangement is by the ratio A + B : X primarily, and according to the decreasing A : B ratio.

The division within the classes may be illustrated by class 2, sulfides, where the following types are given:

Type	*Examples*
1. AmXn where m : n < 3 : 1	tellurobismuthite Bi_2Te_5
2. A_3X	dyscrasite Ag_3Sb
3. A_2X	chalcocite Cu_2S
4. A_3X_2	maucherite $Ni_{11}As_8$
5. A_4X_3	dimorphite As_4S_3
6. AX	galena PbS
7. A_3X_4	linnaeite Co_3S_4
8. A_2X_3	stibnite Sb_2S_3
9. AX_2	pyrite FeS_2
10. AX_3	skutterudite (Co, Ni) As_3

Another illustration would be, class 7, multiple oxides:

Type	*Examples*
1. ABX_2	diaspore $HAlO_2$
2. AB_2X_4	spinel $MgAl_2O_4$
3. AB_4X_7	plumboferrite $PbFe_4O_7$
4. ABX_3	perovskite $CaTiO_3$
5. A_2BX_5	pseudobrookite Fe_2TiO_5
6. AB_2X_5	zirkelite (Ca, Fe, Th, U) $(Ti, Zr)_2O_5$
7. AB_3X_7	coronadite $MnPbMn_6O_{14}$

Those responsible for collections of minerals will find the system of numbers adopted for the different species much more flexible and significant than the scheme used in previous editions. The first integer in a mineral number is the class number. Thus all elements would begin with 1, all sulfides with

2, etc. Under each class, numbers are further assigned according to type. Thus among the sulphides, class 2, the A_2X type would be 23, and class 2, the A_3X_2 type would be 24. Under class 2, type 3, one finds the isometric division 231 and the non-isometric division 232. In the non-isometric division chalcocite is the first mineral with the number 2321. Stromeyerite, the second mineral, in the same division has the number 2322. In general, group numbers contain three figures and mineral numbers four figures. It is unlikely that any number for a species will have more than five digits. Doubtful minerals are not numbered.

A considerable divergence from the sixth edition will be noted on reference to crystallographic data. The angular coordinates consisting of the azimuth phi (ϕ) and the polar distance rho (ρ) are given in recording the crystal angles. The morphological unit has been verified by the unit cell as determined by X-ray measurement. The angles and their significance are illustrated in figures drawn for each system. The table of forms and angles includes all the common forms with letters and important angles. It is particularly adapted to work with the two circle goniometer and the gnomonic projection. One gains the impression that Professor Palache has contributed a wealth of material to the assembly of data for this phase of the subject. Many new crystal drawings have been used and a number of the old figures omitted. The figures used demonstrate careful selection.

The suggestions of Schaller (1930) published in the *American Mineralogist* are followed in the use of the suffix for the adjectival ending of chemical elements used as modifiers of mineral names. The single suffix ian (or oan to indicate a lower valence) is used for example to furnish such words as manganoan, cobaltian, nickelian, mercuroan, or mercurian. Other examples illustrating the form of suffix used would be aluminian, ferroan, ferrian, barian, bromian, carbonian, silician, hydrogenian, antimonian, arsenoan, and arsenian. Mineralogists used to manganiferous, cobaltiferous, nickeliferous, etc. would do well to consult the background of discussian relating to the selection of the suffix which has been carefully absorbed in the New Dana. As used, arsensulfurite is mentioned as an arsenian variety of sulfur, argento-algodonite is an argentian compound, and a copper-bearing variety of argentite is described as cuprian.

Names for varieties of minerals follow the scheme proposed by Schaller. Old names are considered as synonyms. Thus *freibergite* is a synonym for *argentian tetrahedrite; hatchettolite, uranpyrochlor,* and *ellsworthite* are considered as synonyms for the varietal term *uranian pyrochlore.*

The reader is referred to the basic principles of nomenclature so well set forth in the introduction to the fifth and sixth editions. The authors justifiably deviate from the proposal to modify thirty mineral names all well established in the literature by adding *ite,* even granting the possibility of making the change without obscuring the derivation or euphony. Thus familiar names such as cinnabar, diaspore, glaucodot, etc. remain and do not change to cinnabarite, diasporite, glaucodotite, etc.

The Greek letters alpha, beta, gamma, epsilon, and omega, so common to optical descriptions, are not used. These are avoided, it is explained, in order

to save confusion since the first three are "much overworked as designations for physical constants." The optical properties of diaspore may be selected as an illustration of a biaxial mineral.

Orientation		n_{Na}	
X	*c*	1.702	Bx. pos. (+)
Y	*b*	1.722	$2V$ 84–85°
Z	*a*	1.750	$r < v$, weak

The tabulation for brucite, a hexagonal mineral, would be as follows:

O	*E*	
1.559	1.580[s]	Uniaxial pos. (+)
1.59	1.60	Anal. 5, manganoan.

Those interested in the study of ores will welcome the inclusion of data on opaque minerals as they appear on polished surfaces. The reflection percentages of color and references to anisotropism should prove useful. In some cases it would seem even more data could have been included to advantage.

The sections on occurrence have been revised with care and contain an abundance of useful information. Many important minerals have from one to three pages devoted to an excellent and up-to-date summary.

Under the heading *artificial* will be found a summary of the more recent attempts at mineral synthesis. While occasional readers might wish in some instances to have the data correlated more directly with the references, in most cases the proper references are either given directly or are sufficiently apparent. Students of the processes of mineral formation will find much of value under this heading.

The chemical analyses included have been selected carefully, greater emphasis being placed upon more recent studies. More analyses were recorded in the sixth edition and the authors expect the readers to refer to these. In many cases it is presumed that the analyses omitted were incomplete, perhaps so old as to be unreliable, or may have been made on material since shown to be doubtful. With copies of the sixth edition still available analyses omitted may be quickly verified.

One of the most important contributions of the New Dana, a feature not possible in the older editions, is the section under each mineral on the structure cell. Here, where possible, the space group is given using the Hermann-Mauguin notation as utilized in the International Tables for the Determination of Crystal Structures. The names of the crystal classes follow Rogers (1937). The dimensions of the unit cell and the formula based on the structure are also included. References to X-ray studies of various sorts included in the section on references are equally valuable. This information as a whole will find widespread utilization.

One would hardly expect a new edition containing such a great volume of material to be entirely free from errors. On pages 309 and 311 the same

analysis from the Hudson Bay mine at Cobalt is repeated both as an example of rammelsbergite and pararammelsbergite. Further checking would have indicated that the analysis belonged to material shown by Peacock to be pararammelsbergite and thus should appear only under the description of that mineral. It is also assumed that niccolian as used on pages 344 and 345 should be nickelian. Such errors are rare, and Professor Palache has stated in the preface that readers would confer a favor by pointing out any they discern.

In contrast to the sixth edition the seventh edition is printed with larger type but on a somewhat smaller page. The printed area of the page in the preceding edition measured 5 x 8 inches, while the corresponding area for the latest edition is 4½ x 7¼ inches. Although the difference in page size is not great, the choice of a larger type results in a considerable reduction in the number of words per page. It is estimated by the publishers that the previous volume carried about twenty-five per cent more words per page.

The total number of pages in the sixth edition and three appendices was 1411. Volume I of the Seventh Edition contains 834 pages. From the standpoint of size, Volume I of the seventh edition represents a considerable increase in content over the corresponding one-third of the preceding complete volume.

In conclusion it is but proper to congratulate the authors upon the excellent way in which they have maintained the Dana tradition. It is to be hoped that the opportunity will soon come for a resumption of work on the two remaining volumes and that before long an entirely completed seventh edition will be available. The first volume offers assurance that the three together will constitute a valuable summary of mineralogical literature.

COLUMBIA UNIVERSITY,
NEW YORK, N. Y.,
September 15, 1944.

MEMORIAL TO HARRY BERMAN.

CHARLES PALACHE.

HARRY BERMAN, Associate Professor of Mineralogy and Curator of the Mineralogical Museum at Harvard University, was instantly killed in the crash of a transport plane at its landing place, Prestwick, Scotland, on August 27th, 1944. His body now lies in the American cemetery in Cambridge, England, with the mourned and honored dead of the war.

Berman was forty-two years old and was at the height of his productive powers. The loss of my close scientific associate brings bitter sorrow, intensified by the breaking of the close personal relations which have existed between us for two decades.

Harry Berman came to Harvard in 1924 as Assistant to the Curator of the Mineralogical Museum. His knowledge of mineralogy was slight but he seemed to have an instinctive love for the science and threw himself into its study and his work with intense enthusiasm. The Museum was just beginning a period of rapid growth due to the acquisition of abundant funds, and Berman was engaged in rearranging the public exhibitions and improving their installation. He took such courses in the Department as he could find time for and attended evening classes at the Lowell Institute in Boston, gradually building up the course basis for the degree of Adjunct in Arts in 1931. He early developed extreme facility in the methods of optical determination of the nonopaque minerals in loose grains under the microscope and so effectively assisted Professor Esper S. Larsen in the revision of the data of his determination tables that the second edition was issued under their joint authorship in 1934.

Berman was an enthusiastic and indefatigable field worker. He returned from a collecting trip to Mexico, made jointly with Dr. Foshag of the U. S. National Museum in 1927, with a wealth of material, chief of which was a group of giant gypsum crystals from Naica. The removal of these crystals from the cave eight hundred feet underground, where they had formed, was no small task considering their size, their fragile nature and the ignorant workmen he had to employ. But the half ton of crystals was removed almost uninjured and arrived safely in Cambridge where they were mounted in their original positions and form the unrivaled centerpiece of the Museum exhibition hall. He had a passion for collecting large specimens, especially when they showed their mode of implacement in the rock. His latest acquisition for the Museum was a great slab of rock from Arkansas coated with hundreds of quartz crystals, which weighed upwards of a ton and still reposes in the basement in its crate as it arrived.

Berman early perceived that progress in the adequate description and classification of minerals required the knowledge to be derived from their study with X-rays. To prepare himself to equip a laboratory for this study he

took courses under Dr. Warren at the Massachusetts Institute of Technology and was granted a fellowship for travel abroad in 1932–33. He spent part of the year in the laboratory of V. M. Goldschmidt in Göttingen and a more productive period in England, where he became the student of J. D. Bernal at Cambridge. Filled with enthusiasm for the possibilities of X-ray methods, he returned to Harvard and began to collect apparatus and to set it up with his own hands. Both funds and assistants were inadequate, but in the course of the second year he was obtaining results which, as they improved with his hard-won knowledge of operating the complex instruments, gave him intense satisfaction. The analysis and interpretation of his X-ray photographs led him on another track. Some way had to be found of determining accurately the specific gravity of small crystals or fragments of minerals. As the result of endless trials of different methods, he discovered the possibility of adapting to his purpose a torsion balance then on the market. The resulting Berman microbalance may now be found in many research mineral laboratories as an indispensable tool with which the specific gravity of minute single crystals weighing as little as 5 milligrams may be obtained.

Working with graduate students Berman extended the range of high-index liquids for immersion mounts. With Larsen he worked to improve the liquids for gravity separation of mineral grains. Although he did not actively enter the expanding field of microscopic study of opaque minerals, he studied the methods and never failed to use them through others to establish the purity of samples to be analyzed. The formation of a standard collection of X-ray powder photographs was furthered by him as a cherished objective. His goal was so to improve methods of selection of a sample and its investigation that all the physical data of a mineral should be based on homogeneous material of known composition.

His work with Bernal had impressed upon him the part that the new science of crystal chemistry was to play in the developing science of mineralogy. His doctoral thesis, completed in 1936, was a classification of the silicate minerals based upon the work of the English and German X-ray specialists. Less than fifteen per cent of the silicate species had then actually been the subjects of detailed structural studies. Berman's speculations as to the place in the system of the unstudied species have been found to be well grounded and his classification is sound.

The author of this memorial was for many years preceding 1937 engaged in a desultory fashion in collecting data for a new edition of Dana's System of Mineralogy. His chief assistants in this work were Berman, Dr. L. LaForge and Dr. M. A. Peacock, who had first come to Harvard as a Commonwealth Fellow in 1926. In 1936 The Geological Society of America supported with a large grant the project of preparing the new edition of the System with the help of adequate assistants, proposed by Professor Ford of Yale University and the writer. Berman and Peacock were thereupon engaged to give their full time to this work. After a year of preliminary work to establish the form in which the matter should be presented, Dr. Peacock withdrew to accept a position elsewhere. Berman carried on alone for a short time but soon brought Dr. Clifford Frondel to his aid. For the next three years these men

were steadily at work, aided by others to be sure; but in the main Berman wrote the text of the new System. It was early seen that the four-year term of the grant was far too short an allowance of time. As a matter of fact, the year 1941, when the grant came to an end, saw the completion of the manuscript for the first volume only of the proposed three-volume work. It is this volume, appearing from the press only a few weeks before Dr. Berman's death, which is the subject of Professor Kerr's review. This book is essentially Berman's work and will be his lasting memorial.

When the United States entered the World War, Berman gradually became absorbed in consultative work connected with minerals essential to the war effort. He was engaged in field work and laboratory testing relating to optical fluorite, optical calcite, industrial diamonds and quartz. He was successful in finding new or undeveloped sources of the first two minerals and in directing the technical operation of sawing and polishing oriented plates of calcite. For the last year or more he was wholly absorbed in the many scientific problems involved in the cutting of quartz-crystal oscillators, having become Director of Research and Technical Advisor for the Reeves Sound Laboratories and the affiliated Hudson American Corporation. It was through this employment that he came to be on his way to England in August, his services as consultant having been engaged for similar work sponsored by the British Government.

Berman gave no courses of formal instruction at Harvard. Informally he was always at the service of graduate students and was never too busy to leave his own research in order to help anyone who came to seek his aid. In the letters of condolence that have come from widely scattered former students, the most-stressed notes are his cheerful spirit and his kindness. He was the friend and counselor of the student rather than the teacher.

Berman's status at Harvard was as Museum Assistant and Research Associate until in 1940 he received the faculty appointment and Curatorship already stated. He was married in 1926 and his wife and two children survive him. Both Mrs. Berman and young Robert were familiar figures in the "Dana" laboratory, where they assisted materially in assembling reference data for study.

Detailed statement of Berman's publications will doubtless appear elsewhere. In concluding this account of the development of his scientific career, I think I cannot do better than to quote the concluding paragraph of a Bulletin prepared by Professor Kirk Bryan and sent out on September 8th to members and former students of the Division of Geological Sciences of Harvard University.

"The Division of Geological Sciences shares with you what little we know about Berman's death. Our sense of loss of a friend, a comrade and a patriot is very great. We have given herewith an outline of his scientific career. We cannot, however, revive his enthusiasm for science, his dispassionate judgment or his kindly and helpful ways. Those of you who were honored by his friendship will supply, in imagination, what this account so obviously lacks."

HARVARD UNIVERSITY,
October 13, 1944.

DISCUSSION AND COMMUNICATIONS

LEACHED OUTCROPS.

Sir: I have received my copy of *Economic Mineral Deposits,*[1] and have perused it in a general way. On the whole I approve of your manner of presentation. Lindgren's and Emmons' classifications were useful and have served their purpose, but they were not wholly satisfactory. Neither is yours, but it seems a more logical plan for presentation than theirs for the person following geology in the field.

Probably no book classification of mineral deposits can be adequate, because so many varieties of mineral occurrence overlap. An old hand in the field thinks of a district as a unit, and fits all of its various types of ore occurrence into a kaleidoscopic compound from which shapes are drawn to fit the viewpoint held at a particular moment. A textbook cannot do that without bringing on chaos. I think your effort however, in classifying deposits from the standpoint of processes, trends in that direction so far as textbook limitations permit.

Your treatment of leached outcrops is easily the most complete and intelligible thus far presented in a textbook. It contains various flaws which are not directly attributable to you; they must be debited against our failure, thus far, to have edited in a unified way the mass of leached outcrop data presented since 1926.

An example is your implied limitation of specific limonitic types to particular sulphides. Boxworks, for example, may form from any sulphide or other mineral which occurs in massive form and possesses a through-going cleavage or fracture system. Only by recognizing in the boxwork pattern a pseudomorph of the cleavage or fracture pattern characteristic of the particular sul-

[1] Bateman, Alan: Economic Mineral Deposits. John Wiley & Sons, New York, 1942.

phide, or other mineral (such, for example, as calcite or fluorite), and recognizing the accessory indigenous limonitic products which go with the boxwork in a given case, can the occurrence be intelligently interpreted. Most sulphides, in fact, yield both cellular boxwork and cellular sponge derivatives in addition to other limonitic types, though one or the other type usually predominates. That fact was not made clear in some of the earlier papers because we were not aware of it at that time.

Relief limonite is that in which the particles stand out in distinct relief, in contrast with the frequent flat or crusted surfaces. The term was coined originally by Boswell and myself to distinguish in the field the limonitic products in which pseudomorphic detail was largely obliterated but enough of it preserved to contrast with transported material. In indigenous derivatives from massive sulphide (other than pyrite) relief limonite almost invariably contains ghosts of the cellular structure emerging dimly through the pulverulent or partly-compacted limonite. But in disseminated chalcocite deposits the cellular structure often is absent and always is fragile; and in such case the relief usually depends upon the fact that each chalcocite-pyrite grain oxidizes more or less by itself, and the limonitic granules, as produced, tend to build upon one another instead of coalescing into a crusted product. There thus is preserved the characteristic of relief, which aids in identification of the product as a derivative from a potentially useful sulphide.

When Locke wrote his book he limited the field to disseminated copper deposits, but failed to define his corresponding limitation in use of the term. Relief limonite may mean chalcocite, covellite, bornite (possibly but not usually chalcopyrite), sphalerite, galena or other sulphide. Whether relief limonite, cellular boxwork, or other limonitic type forms depends upon the sulphur-iron ratio involved in the oxidation, composition of the ground water, proximity to water level at the time of oxidation, and a host of other factors, all interrelated. The term is in no sense restricted to chalcocite-covellite-bornite deposits. As a rule some clue outside the particular relief limonite involved must exist before the relief

product in any given case may be ascribed with confidence to a chalcocite or other origin.

Color in limonite as a guide to the parent mineral likewise is much more deceptive than your list implies. The Indian-reddish color, in the derivatives of chalcopyrite for example, is almost exclusive in some districts, although the orange-ochreous color is more characteristic in most of them.

After the war I hope to bring all the leached outcrop data together, outline the skeleton framework which underlies the various cellular classifications and other limonitic types, assign each product to its proper position within the framework, and present a unified and comprehensive picture. I congratulate you upon having made, in the meantime, a bold and creditable start in that direction, even though in some respects you may have been misled, through no fault of your own, from a perusal of the incomplete literature thus far published.

ROLAND BLANCHARD.

MOUNT ISA, QUEENSLAND, AUSTRALIA,
July 6, 1943.

REVIEWS *

Experimental Spectroscopy. By RALPH A. SAWYER. Pp. viii + 323; Figs. 107. Prentice-Hall, Inc., New York. Price, $5.00; text $3.75.

This volume is largely a discussion of the general principles, construction, and use of spectrographic and auxiliary apparatus. The various types of prism and grating spectrographs, photometers, and comparators are explained in some detail. There are also chapters on the photographic process and the determination of wave length and of spectral intensity.

The emphasis is placed on the basic theories and techniques "that are fundamental to practically all uses of spectroscopic equipment." There is much material bearing on the adaptability and limitations of this equipment.

BOOKS RECEIVED.

RALPH E. DIGMAN.

Dana System of Mineralogy. Seventh edition, Volume I, Elements, Sulfides, Sulfosalts, Oxides. By CHARLES PALACHE, HARRY BERMAN, AND CLIFFORD FRONDEL. Pp. xiii + 834. John Wiley and Sons, New York, 1944. Price, $10.00. *See review by Professor Kerr elsewhere in this number of the Journal.*

Petroleum Development and Technology, 1944. Am. Inst. Mining and Metallurgical Engineers, Transactions, Vol. 135. Petroleum Division. Pp. 581. The Maple Press, York, Pa., 1944.

Canadian Mines Handbook, 1944. Pp. 272. Northern Miner Press, 122 Richmond St. W., Toronto. Price, $1.00. *A full report of the developments, etc., of the mineral industries of Canada. In two parts: Principal companies, and Supplementary list—inactive and extinct companies.*

Illinois Geological Survey. Urbana, 1944.

Bull. 68. **Some Addresses and Papers Presented at the Dedication of the State Natural Resources Building.** Pp. 305; Figs. 92. *A bound volume of papers discussing topics such as coal, oil and gas, industrial minerals, and Devonian stratigraphy.*

Rept. of Investigations—No. 93. **Progress Reports on Subsurface Studies of the Pennsylvanian System in the Illinois Basin.** Pp. 87; Figs. 12; Pls. 5.

Rept. of Investigations—No. 96. **Differential Thermal Analysis of Clays and Shales, A Control and Prospecting Method.** R. E. GRIM AND R. A. ROWLAND. Pp. 23; Figs. 17.

Rept. of Investigations—No. 98. **Smaller Foraminifera from the Porters Creek Formation (Paleocene) of Illinois.** CHALMER COOPER. Pp. 10; Figs. 2; Pls. 2.

* Books noted under *Reviews* and *Books Received* may be ordered through the Economic Geology Bookshop, M. M. Leighton, Urbana, Ill., but orders for official reports and single copies of Journals should be sent directly to their publishers.

Rept. of Investigations—No. 99. **Domestic Coke from Illinois Coals, An Experimental Sole-heated Oven.** FRANK REED AND HAROLD JACKMAN Pp. 12; Figs. 3.

Press Bull.—No. 49. **Developments in Eastern Interior Basin in 1943.** ALFRED H. BELL. Pp. 8; Fig. 1.

Press Bull.—No. 50. **Oil and Gas Development in Illinois in 1943.** ALFRED BELL AND CHAS. CARTER. Pp. 38; Figs. 3.

Summarized Records of Deep Wells. R. C. TUNKER. Pp. 938; Two Maps, wells on the Charleston, Kenna, and Ripley quadrangles (1:62,500) and wells for entire state (1:250,000). West Virginia Geol. Surv., Vol. XVI. Charleston, 1943.

Careers and Mineral Industries. Penn. State College Bull., Circular 17. Pp. 24; Figs. 34. State College, 1944.

High Alumina Iron Ores in Washington County, Oregon. F. W. LIBBEY, W. D. LOWRY, AND R. S. MASON. Pp. 23; Figs. 9. Oregon Dept. of Geol. and Mineral Industries, Short Paper No. 12. Portland, 1944. Price, 15 cents.

Antimony in Oregon. N. S. WAGNER. Pp. 20; Figs. 4. Oregon Dept. of Geol. and Mineral Industries, Short Paper No. 13. Portland, 1944. Price, 15 cents.

Dept. Nacional da Producao Mineral, Brazil.

Boletim No. 55. **Zirconio em Pocos de Caldas.** E. A. TEIXEIRA. Pp. 63; Figs. 8; Pls. 15. 1943.

Boletim No. 56. **Brasil, 1942, Recursos Minerais.** Pp. 73; Pl. 1. 1943.

Boletim No. 57. **Relatorio da Diretoria, 1940.** O. BARBOSA AND GLYCON DE PAIVA. Pp. 95; Pls. 2. 1943.

Avulso No. 49. **O Codigo de Minas e o Incremento da Mineracao no Brasil em 1941.** JOSE ALVES. Pp. 48. 1943.

Avulso No. 50. **Cromo em Piui, Minas Gerais.** H. C. A. DE SOUSA. Pp. 23; Figs. 6; Pls. 2. 1943.

Avulso No. 51. **Informacoes Sobre Aparelhos e Dispositivos Para Extra de Ouro de Aluviao.** D. GUIMARAES. Pp. 20; Figs. 14. 1942.

Avulso No. 53. **Mica na Regiao de Sta. Maria do Suassui, Minas Gerais.** THOMAS MURDOCK AND CHAS. HUNTER. Pp. 27; Pls. 2. 1944.

Avulso No. 54. **Mica no Estado de Sao Paulo.** THOMAS MURDOCK. Pp. 30; Figs. 3; Pls. 4. 1944.

Avulso No. 55. **Cristal de Rocha no Estado do Espirito Santo.** FRED. KNOUSE. Pp. 16; Figs. 2; Pls. 7. 1944.

Avulso No. 56. **Abecedario do Prospetor de Mica.** DONALD D. SMYTHE. Pp. 22; Figs. 5. 1944.

Etudes Geologiques sur le Sahara. I. A la mémoire de Fernand Jacquet. M. GIGNOUX, **II. Nouvelles observations sur les fulgurites du Sarhara.** A. LACROIX, **III. La géologie des confins de la Mauritanie septentrionale d'aprés les travaux de Fernand Jacquet.** N. MENCHIKOFF AND M. NICKLES, **IV. Contribution à l'étude pétrographique des roches cristallines et métamorphiques de la Mauritanie.** E. JÉRÉMINE, **V. Sur quelques roches du tasiast.** E. JÉRÉMINE, **VI. Note prélininaire sur les roches éruptives et métamorphiques recuellies par Fernand Jacquet dans de le Sahara Occi-**

dental. E. JÉRÉMINE, AND M. NICKLES, **VII. Etude pétrographique des sédiments du Sahara occidental.** C. DARLES. Pp. 191; Figs. 2; Pls. 17. Bulletin du Service des Mines, No. 6. De l'Afrique Occidentale Française. Dakar, 1942.

Etudes Stratigraphiques et Paleontologiques sur le Bassin du Niger. I. Note stratigraphique sur le Crétacé supérieur du Damergou. R. LAMBERT, **II. Vertébrés fossiles du Bassin du Niger.** C. ARAMBOURG AND L. JOLEAUD, **IV. Invertébrés du Crétacé supérieur du Damergou, Territoire du Niger.** D. SCHNEEGANS. Pp. 143; Fig. 18; Pls. 7. Bulletin du Service des Mines, No. 7. De l'Afrique Occidentale Française. Dakar, 1943.

Sur la Stratigraphie, la Lithologie et la Structure du gisement Cuprifere de l'Etoile du Congo. A. JAMOTTE. Pp. 77; Figs. 8. No. 3. Bulletin d'Etudes et d'Informations, Association des Ingenieurs de la Faculte Technique du Hainaut, Section Congolaise. Elisabethville, 1943.

The Geology of the Nsuta Manganese Ore Deposits. H. Service. With Appendix: **Microscopical Features of Some Specimens of Gold Coast Manganese Ores.** J. A. DUNN. Pp. 32; 5; Pls. 15. Mem. No. 5, Gold Coast Geol. Surv., 75 Cornwall Gardens, S. Kensington, London, S.W. 7. 1943. Price, 6 s.

SOCIETY OF ECONOMIC GEOLOGISTS

The following notice was transmitted to the membership by mail, as of August 17.

NOTICE OF NOMINATIONS FOR OFFICERS.

The Nominating Committee, consisting of J. A. Noble, Chairman, R. C. Allen, and W. E. Wrather, presents the following nominations for office:

President for 1946	*First Vice-President for 1946*
W. O. Hotchkiss	J. Terry Duce

Councilors for 1945–1947

Francis Cameron — George M. Fowler — Thomas G. Moore

Regional Vice-Presidents for 1945

Rene A. Pelletier	For *Africa*	Alfred Brammall	For *Europe*
M. J. S. Krishnan	For *Asia*	George Hanson	For *North America*
Robert L. Jack	For *Australia*	O. H. Leonardos	For *South America*

The list of nominees is subject to additions proposed by the membership at large, in accord with Section 16 of the By Laws, which states:

> "Any further nomination or nominations proposed and supported in writing by ten or more members shall, if received by the Secretary within seventy-five days, be added to the official ballot."

Any additional nominations made in accordance with the foregoing provisions will appear on the regular ballot. The period for additional nominations closes on October 31, 1944, and such nominations must be received by the Secretary before or on that date.

Attention of the membership is especially directed to the need for prompt action if substitute nominations are contemplated.

Chas. H. Behre, Jr., *Secretary.*

Department of Geology,
Columbia University,
New York City, U. S. A.,
August 17, 1944.

The Council of the Society of Economic Geologists has accepted the cordial invitation of the American Institute of Mining and Metallurgical Engineers to meet jointly with the Institute for such sessions as are of mutual interest. The dates of the technical sessions will be February 19–22, 1945, in the Pennsylvania Hotel, New York City. Members are invited to present papers dealing with any

phase of applied geology,—ore deposits, industrial minerals, fuels, ground water, engineering geology, applied geophysics, and mineral economics. Joint sessions will be held with the Mining Geology Committee and with the Industrial Minerals Division of the Institute. Members wishing to present papers should address the office of the Secretary, 411 Schermerhorn Hall, Columbia University, New York 27, N. Y., for the usual abstract forms. No titles will be accepted after December 15, 1944. The Program Committee has been authorized to arrange for a program commensurate with the time available for the sessions and with the best interests of the Society.

Program Committee,

H. E. McKinstry, *Chairman*
M. H. Gidel
James Gilluly
A. I. Levorsen
V. T. Stringfield
C. H. Behre, Jr.

SCIENTIFIC NOTES AND NEWS

VICTOR M. LOPEZ, Director of Mines and Geology, the United States of Venezuela, has been commissioned by the Government of Venezuela to cooperate with the Government of the Republic of Haiti on geologic work. For this purpose Dr. Lopez will spend a short time in Haiti.

GEORGE B. CRESSEY, Chairman of the Department of Geology and Geography at Syracuse University, delivered the Second Series of Haas Commemorative Lectures at Northwestern University, Evanston, Illinois, on October 19 and 20, 1944. This series of lectures has been established in honor of Dr. W. H. Haas, Professor Emeritus of Geography, who retired from active service some years ago. The three lectures given by Dr. Cressey were entitled, "Report from Asia," "How to Defeat Japan," and "Pictures from China." They were enthusiastically received by the audience of townspeople, students, and University faculty.

A. L. HOWLAND and R. M. GARRELS have been released from their teaching duties in the Department of Geology and Geography at Northwestern University for the duration of the war, and are engaged in special research in Washington.

J. T. STARK, Chairman of the Department of Geology and Geography at Northwestern, has been on leave of absence since April, 1943. He now holds the rank of Major in the Army Air Forces, and is connected with the Arctic, Desert and Tropic Information Center at Orlando, Florida.

ROBERT P. SHARP has been appointed Associate Professor of Geology at the University of Minnesota, where he will have charge of the Division of Glaciology and Geomorphology. He is now commissioned Captain in the Army Air Corps, and is connected with the Army Arctic Information Center. At present he is conducting field observations for the Army in the arctic northwest.

WALTER HARVEY WEED, consulting geologist, well known for his work on the ore deposits of Butte, Montana, and other western mining districts, died on September 5, 1944, at Los Angeles.

JOHN H. MEANS of Canaan, Indiana, died on January 2, 1944. He was a charter member of the Society of Economic Geologists.